Supporting Information

Novel Synthesis of Divergent Aryl Imidazoles from Ketones Involving Copper-Catalyzed α-Amination and Oxidative C-C Bond Cleavage

Jiangkun Huang,[a] Lan Luo,[a] Naiguo Xing,[a] Linghui Gu,[a] Chen Li,[a] Qiao Han,[a] Shilong Zheng,*[b] Ling He*[a]

[a]Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, Sichuan Engineering Laboratory for Plant-Sourced Drug and Sichuan Research Center for Drug Precision Industrial Technology, Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University, Chengdu, Sichuan, 610041(P. R. China). E-mail: heling2012@scu.edu.cn.

[b]Department of Chemistry and RCMI Cancer Research Center, Xavier University of Louisiana, New Orleans, LA 70125, USA.

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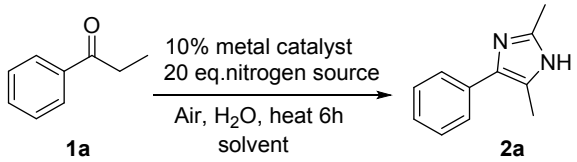
1. General information

All reactions were carried out under air atmosphere, unless otherwise mentioned. Commercially available materials were used as received without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates using UV light as a visualizing agent . Commercial silica gel was used for column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz spectrometer. ^{1}H NMR spectra were referenced to Chloroform-d(7.26 ppm)or DMSO-d_6(2.50 ppm), and reported as follows; chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to Chloroform-d (77.23 ppm) or DMSO-d_6(39.51 ppm). Mass spectral data were obtained from Bruker Daltonics Data analysis 3.2 mass spectrometer.X-Ray data were collected on a Bruker APEX-II equipped with a CCD area detector using Mo/Kα radiation. The structures were solved by direct method using SHELXL-97.

2. Optimization of the reaction conditions(Table 1)



Entry	Catalyst	Solvent	nitrogen source	Temp (°C)	Yield (%)
1	-	MeOH	$(NH_4)_2CO_3$	60	0
2	CuI	MeOH	$(NH_4)_2CO_3$	60	59
3	$Cu(OTf)_2$	MeOH	$(NH_4)_2CO_3$	60	25
4	CuCl	MeOH	$(NH_4)_2CO_3$	60	23
5	CuBr	MeOH	$(NH_4)_2CO_3$	60	40
6	CuI	MeOH	$(NH_4)_2CO_3$	40	trace
7	CuI	MeOH	$(NH_4)_2CO_3$	80	65
8	**CuI**	**MeOH**	**$(NH_4)_2CO_3$**	**100**	**76**
9	CuI	*n*-BuOH	$(NH_4)_2CO_3$	100	39
10	CuI	EtOH	$(NH_4)_2CO_3$	100	47
11	CuI	MeOH	NH_4OAc	100	0

12	CuI	MeOH	$(NH_4)_2C_2O_4$	100	trace

Reaction conditions: catalyst (10 mol%), **1a** (0.37 mmol), nitrogen source (7.4 mmol), air, and solvent (2 mL).

First, using propiophenone as the substrate, we investigated the effect of different reaction conditions on the reaction. The alcohol was beneficial to the reaction. As shown in Table 1, methanol was the most effective for the cleavage and the reaction was hardly carried out in ethyl acetate, MeCN, DCM, dioxane, DMF or DMSO. Besides copper salt, $FeCl_2$, $Rh_2(OAc)_2$, Ru(TTP)(CO) were employed as promoter for the cleavages of 1a in methanol. However, only cuprous iodide can obtain moderate to high yield in promote cleavage reaction. In addition,the influence of the ammonium salt as nitrogen source on the α-amination reaction of 1a has been studied using ammonium carbonate, ammonium acetate and ammonium oxalate. Table 1 shows the other optimal reaction conditions include CuI as the catalyst, $(NH_4)_2CO_3$ as the nitrogen source, and air as the oxidant at 100°C in a sealed tube for 6 h(Table 1,entry 8).

3. General procedure for the formation of compound 2

General procedure for the formation of compound 2: A 25ml sealed tube was charged with CuI (10 mol%), 1 (0.37 mmol), $(NH_4)_2CO_3$ (7.4 mmol), and MeOH (2 mL,undried), H_2O(0.37mmol) ,the mixture was stirred at 100℃ for 6~24h. After disappearance of the reactant (monitored by TLC), the reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The crude residue was purified by silica gel chromatography using petroleum ether/acetone /triethylamine as eluent to give pure product 2.

2,5-Dimethyl-4-phenyl-1H-imidazole (2a): White soild, yield: 76%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.16 (t, *J* = 7.7 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.3, 134.8, 128.9, 128.6, 125.7, 125.4, 13.9, 12.3. HRMS (ESI) calcd for $C_{11}H_{13}N_2$ $[M+H]^+$: 173.1073, Found 173.1072.

4-(4-Chlorophenyl)-2,5-dimethyl-1H-imidazole (2b): White soild, yield: 56%. ^{1}H NMR (400 MHz,DMSO-d_6) δ 11.70 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.8 Hz, 2H), 2.31 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.4, 134.5, 129.7, 128.5, 127.2, 113.7, 13.9, 12.1. HRMS (ESI) calcd for $C_{11}H_{12}ClN_2$ $[M+H]^+$: 207.0684, Found: 207.0682.

4-(4-Bromophenyl)-2,5-dimethyl-1H-imidazole (2c): White soild, yield: 54%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (s, 1H), 7.52 (s, 4H), 2.30 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.5, 137.3, 134.6, 131.4, 127.8, 127.6, 118.2, 14.0, 12.2. HRMS(ESI) calcd for $C_{11}H_{12}BrN_2$ $[M+H]^+$:251.0178, Found: 251.0181.

4-(4-Fluorophenyl)-2,5-dimethyl-1H-imidazole (2d, CCDC 1853653): White soild, yield: 80%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 – 7.48 (m, 2H), 7.11 – 7.04 (m, 2H), 3.96 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 160.6 (d, *J* = 241.9 Hz), 142.5, 131.9, 127.7 (d, *J* = 7.7 Hz), 115.5 (d, *J* = 21.2 Hz), 14.1, 12.2. HRMS (ESI) calcd for $C_{11}H_{12}FN_2$ $[M+H]^+$: 191.0979, Found 191.0973.

4-(2-Fluorophenyl)-2,5-dimethyl-1H-imidazole (2e): White soild, yield: 76%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.49–7.43 (m, 1H), 7.21 (m, 1H), 7.16–7.04 (m, 2H), 6.28 (s, 1H), 2.35 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 159.0 (d, *J* = 245.7 Hz), 143.5, 130.0 (d, *J* = 3.8 Hz), 129.9, 128.3 (d, *J* = 8.3 Hz), 124.8, 124.3 (d, *J* = 3.3 Hz), 120.7 (d, *J* = 14.1 Hz), 115.9 (d, *J* = 22.7 Hz), 13.9, 12.4 (d, *J* = 3.6 Hz). HRMS (ESI) calcd for $C_{11}H_{12}FN_2$ $[M+H]^+$: 191.0979, Found: 191.0978.

4-(4-(Trifluoromethyl)phenyl)-2,5-dimethyl-1H-imidazole (2f): White soild, yield: 65%. ^{1}H NMR (400 MHz,DMSO-d_6) δ 11.82 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.8, 140.5, 133.3, 126.3, 126.0, 125.7(125.72), 125.7(125.69), 125.6 (q, *J* = 3.3 Hz), 124.3, 14.2, 11.8. HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2$ $[M+H]^+$: 241.0947, Found: 241.0947.

4-(3-(Trifluoromethyl)phenyl)-2,5-dimethyl-1H-imidazole (2g): White soild, yield: 57%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.82 (s, 1H), 7.91 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 2.36 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz,DMSO-d_6) δ 142.5, 136.3, 129.7, 129.4, 129.1, 128.9, 128.8, 124.4 (q, *J* = 272.3 Hz), 121.6, 121.5, 121.4, 121.3, 13.7, 11.7. HRMS (ESI) calcd for $C_{12}H_{12}F_3N_2$ $[M+H]^+$: 241.0947, Found: 241.0950.

2,5-Dimethyl-4-(p-tolyl)-1H-imidazole (2h): White soild, yield: 41%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.63 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.0, 134.4, 131.9, 129.1(129.11), 129.1(129.08), 125.7, 20.9, 13.9, 12.4. HRMS (ESI) calcd for $C_{12}H_{15}N_2$ $[M+H]^+$: 187.1230, Found: 187.1233.

4-(4-Methoxyphenyl)-2,5-dimethyl-1H-imidazole (2i): White soild, yield: 39%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H), 2.26 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 157.6, 142.1, 127.5, 127.3, 114.2, 55.5, 14.1, 12.5. HRMS (ESI) calcd for $C_{12}H_{15}N_2O$ $[M+H]^+$: 203.1179, Found: 203.1180.

2,5-Dimethyl-4-(thiophen-2-yl)-1H-imidazole (2j): White soild, yield: 42%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.73 (s, 1H), 7.31 (d, *J* = 5.0 Hz, 1H), 7.04 (m, 2H), 2.29 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz,DMSO-d_6) δ 142.4, 127.7(127.68), 127.7(127.65), 122.7, 120.9(120.86), 120.9(120.85), 13.8, 11.4. HRMS (ESI) calcd for $C_9H_{11}N_2S$ $[M+H]^+$: 179.0637, Found: 179.0637.

4-(2,3-Dihydrobenzofuran-5-yl)-2,5-dimethyl-1H-imidazole (2k): White soild, yield: 68%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.59 (s, 1H), δ 7.39 (s, 1H), 7.24 (d, *J* = 8.3 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 4.51 (t, *J* = 8.7 Hz, 2H), 3.18 (t, *J* = 8.7 Hz, 2H), 2.24 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.1, 141.9, 127.7, 125.8, 123.1, 109.1, 71.3, 29.7, 14.2, 12.6. HRMS (ESI) calcd for $C_{13}H_{15}N_2O$ $[M+H]^+$: 215.1179, Found: 215.1178.

2,5-Dimethyl-4-(5,6,7,8-tetrahydronaphthalen-2-yl)-1H-imidazole (2l): White soild, yield: 39%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.60 (s, 1H), 7.23 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 2.71 (m, 4H), 2.27 (s, 3H), 2.23 (s, 3H), 1.73 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.9, 136.5, 133.8, 131.9, 129.1, 126.2, 123.2, 29.2, 28.7, 23.1(23.13), 23.1(23.11), 14.0, 12.5. HRMS (ESI) calcd for $C_{15}H_{19}N_2$ $[M+H]^+$: 227.1543, Found: 227.1538.

4-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-2,5-dimethyl-1H-imidazole (2m): White soild, yield: 41%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.56 (s, 1H), 6.99 (m, 2H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.24 (s, 4H), 2.25 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 143.6, 142.1, 141.7, 128.6, 119.1, 117.4, 114.5, 64.6, 64.5, 14.2, 12.5. HRMS (ESI) calcd for $C_{13}H_{15}N_2O_2$ $[M+H]^+$: 231.1128, Found: 231.1126.

2,5-Diethyl-4-phenyl-1H-imidazole (2n): Colourless oil, yield: 24%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.57 (s, 1H), δ 7.52 (d, *J* = 7.8Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.17 (t, *J* = 7.8Hz, 1H), 2.69 (q, *J* = 7.6Hz, 2H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* =7.6 Hz, 3H), 1.19 (t, *J* =7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.1, 134.9, 128.8, 127.5, 126.4, 125.8, 21.8, 19.6, 14.7, 13.3. HRMS (ESI) calcd for $C_{13}H_{17}N_2$ $[M+H]^+$: 201.1386, Found: 201.1380.

4-Phenyl-2,5-dipropyl-1H-imidazole (2o): Colourless oil, yield: 11%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.12 (s, 1H), δ 7.52 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.68 (m, 4H), 0.92 (m, 6H). ^{13}C NMR (150 MHz, Chloroform-d) δ 147.3, 133.9, 128.4, 127.6, 126.8, 126.1, 30.5, 28.2, 23.1, 22.1, 14.0, 13.8. HRMS (ESI) m/z calcd for $C_{15}H_{21}N_2$ $[M+H]^+$: 229.1699 , Found: 229.1700.

2,4,5-Triphenyl-1H-imidazole (2p): White soild, yield: 48%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.73 (s, 1H), 8.12 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.46 (m, 6H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, DMSO-d_6) δ 145.9, 137.5, 135.6, 131.5, 130.8, 129.1(129.12), 129.1(129.09), 128.9, 128.7, 128.6, 128.2, 127.5, 126.9, 125.6. HRMS (ESI) calcd for $C_{21}H_{17}N_2$ $[M+H]^+$: 297.1386, Found: 297.1388.

4. General procedure for the formation of compound 3

General procedure for the formation of compound 3: A 25ml sealed tube was charged with CuI (10 mol%), Phenylacetone (0.37 mmol), Aldehyde (1.48 mmol), $(NH_4)_2CO_3$ (7.4 mmol), and MeOH (2 mL, undried, hydrous methanol), the mixture was stirred at 100℃ for 6~24h. After disappearance of the reactant (monitored by TLC) , the reaction mixture was filtered and the filtrate was concentrated under reduced pressure.The crude residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate as eluent to give pure product 3.

5-Methyl-2,4-diphenyl-1H-imidazole (3a): Yellow solid, yield: 66%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.39 (s, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.50–7.37 (m, 4H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.2, 134.7, 131.0, 129.2, 128.9, 128.3, 126.6, 126.3, 125.2, 12.5. HRMS (ESI) m/z calcd for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230, Found: 235.1230.

5-Methyl-4-phenyl-2-(p-Tolyl)-1H-imidazole (3b): Yellow solid, yield: 65%.^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (d, *J* = 9.7 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.49–7.39 (m, 2H), 7.31 (m, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.48 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 145.1, 138.5, 133.0, 129.6, 129.3, 128.6, 127.3, 126.7, 126.6, 125.0, 21.3, 12.6. HRMS (ESI) m/z calcd for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1397 , Found: 249.1386.

2-(4-Methoxyphenyl)-5-methyl-4-phenyl-1H-imidazole (3c): Yellow solid, yield: 74%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.28 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 159.8, 145.3, 128.7, 128.5, 128.4(128.41), 128.4(128.35), 126.8, 126.7, 126.4, 123.0, 114.1, 55.3, 12.3. HRMS (ESI) m/z calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335, Found: 265.1337.

2-(2-Methoxyphenyl)-5-methyl-4-phenyl-1H-imidazole (3d): Yellow semisolid, yield: 60%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.46–8.27 (m, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.26 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 155.5, 142.8, 133.3, 129.2, 128.6, 128.3, 126.5, 126.4, 121.6, 118.2, 111.2, 55.8, 12.9. HRMS (ESI) m/z calcd for $C_{17}H_{17}N_2O$ $[M+H]^+$: 265.1335, Found: 265.1337.

2-(Benzo[d][1,3]dioxol-5-yl)-5-methyl-4-phenyl-1H-imidazole (3e): Yellowish solid, yield: 60%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.28 (s, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.48 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* =7.5 Hz, 1H), 6.06 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.1, 147.5, 143.9, 136.3, 136.1, 128.7, 126.4, 126.0, 125.5, 124.2, 118.9, 109.0, 105.5, 101.6, 11.8. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_2O_2$ $[M+H]^+$: 279.1128, Found: 279.1130.

N,N-Dimethyl-4-(5-methyl-4-phenyl-1H-imidazol-2-yl)aniline (3f): Yellow solid, yield: 70%. ^{1}H NMR (600 MHz, DMSO-d6) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 2.94 (s, 6H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 150.4, 145.2, 128.7, 126.4, 126.3, 125.9, 119.3, 112.4, 58.1, 8.2. HRMS (ESI) m/z calcd for $C_{18}H_{20}N_3$ $[M+H]^+$: 278.1652, Found: 278.1651.

2-(3,4-Dimethoxyphenyl)-5-methyl-4-phenyl-1H-imidazole (3g): Yellow solid, yield: 52%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (m, 3H), 7.4–7.34 (m, 3H), 7.24 (d, *J* = 7.3 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-d) δ 149.4, 149.3, 145.1, 132.0, 128.6, 128.5, 127.3, 126.7, 126.5, 123.3，117.2, 111.1, 108.7, 55.9, 55.8, 14.2. HRMS (ESI) m/z calcd for $C_{18}H_{19}N_2O_2$ $[M+H]^+$: 295.1441, Found: 295.1441.

2-(4-Chlorophenyl)-5-methyl-4-phenyl-1H-imidazole (3h): White solid, yield: 51%. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz,2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR

(150 MHz, Chloroform-d) δ 144.2, 134.2, 133.7, 132.8, 128.9, 128.5(128.53), 128.5(128.49), 126.9, 126.8, 126.5, 12.1. HRMS (ESI) m/z calcd for $C_{16}H_{14}ClN_2$ $[M+H]^+$: 269.0840, Found: 269.0842.

2-(3-Chlorophenyl)-5-methyl-4-phenyl-1H-imidazole (3i): White solid, yield: 64%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 (s, 1H), 7.71 (d, *J* = 5.8 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.28 (m, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 143.3, 134.8, 133.3, 132.1, 130.8, 130.1, 128.7(128.69), 128.7(128.66), 127.1, 127.0, 125.4, 123.4, 12.2. HRMS (ESI) m/z calcd for $C_{16}H_{14}ClN_2$ $[M+H]^+$: 269.0840, Found: 269.0843.

5-Methyl-2-(naphthalen-1-yl)-4-phenyl-1H-imidazole (3j): White solid, yield: 91%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.58 (dd, *J* = 6.5, 3.4 Hz, 1H), 7.87–7.80 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.1 Hz, 1H), 7.49 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.44–7.36 (m, 3H), 7.30 (t, *J* = 7.3 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 144.4, 133.8, 133.3, 131.0, 129.2, 128.6, 128.3, 127.8, 126.8, 126.7, 126.6, 126.5, 126.1, 126.0, 124.9, 12.4. HRMS (ESI) m/z calcd for $C_{20}H_{17}N_2$ $[M+H]^+$: 285.1386, Found: 285.1390.

5-Methyl-4-phenyl-2-(thiophen-2-yl)-1H-imidazole (3k): Yellow solid, yield: 51%. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.26–7.18 (m, 2H), 6.96 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ140.8, 133.4, 132.7, 128.9, 128.5, 127.7, 126.9, 126.6, 125.5, 124.1, 12.3. HRMS (ESI) m/z calcd for $C_{14}H_{13}N_2S$ $[M+H]^+$: 241.0794, Found: 241.0796.

5-Methyl-4-phenyl-2-propyl-1H-imidazole (3l): Yellow semisolid, yield: 40%. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.70 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 1H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.37 (s, 3H), 1.71–1.61 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.4, 133.6, 131.2, 128.5, 126.5, 126.1, 30.4, 22.1, 13.9, 12.3. HRMS (ESI) m/z calcd for $C_{13}H_{17}N_2$ $[M+H]^+$: 201.1386, Found: 201.1389.

5-Methyl-4-phenyl-1H-imidazole (3m, CCDC 1882199): Yellowish solid, yield: 78%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.07 (s, 1H), 7.60 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.20 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (150 MHz, CD_3OD+Chloroform-d) δ 133.5, 133.3, 132.2, 128.3, 126.5, 126.2, 11.4. HRMS (ESI) m/z calcd for $C_{10}H_{11}N_2$ $[M+H]^+$: 159.0917, Found: 159.0917.

5. General procedure for the formation of compound 4

General procedure for the formation of compound 4: A 25ml sealed tube was charged with CuI (10 mol%), α-aryl ketone(0.37 mmol), ketone (1.48 mmol), $(NH_4)_2CO_3$ (7.4 mmol), and MeOH (2 mL,undried, hydrous methanol), the mixture was stirred at 100℃ for 6~24h. After disappearance of the reactant (monitored by TLC) , the reaction mixture was filtered and the filtrate was concentrated under reduced pressure.The crude residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate as eluent to give pure product.

3-(2,2-Dimethyl-5-phenyl-2H-imidazol-4-yl)-1H-indole (4a, CCDC 1882198): White solid, yield: 65%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 1H), 8.33–8.26 (m, 1H), 7.63–7.48 (m, 5H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.25–7.12 (m, 2H), 6.91 (d, *J* = 2.9 Hz, 1H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.3, 158.5, 136.5, 135.1, 130.1, 129.0, 128.8(128.84), 128.8(128.78), 126.9, 123.2, 122.4, 121.1, 112.3, 108.4, 101.8, 25.3. HRMS (ESI) calcd for $C_{19}H_{18}N_3$ $[M+H]^+$: 288.1490, Found: 288.1492.

3-(2,2-Dimethyl-5-phenyl-2H-imidazol-4-yl)-2-methyl-1H-indole (4b): White solid, yield: 75%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.42 (s, 1H), 7.91–7.82 (m, 1H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.30 (m, 3H), 7.03 (m, 2H), 6.83 (t, *J* = 7.6 Hz, 1H), 2.10 (s, 3H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.8, 159.8, 137.3, 135.7, 133.7, 130.4, 128.8, 128.4, 127.6, 121.5, 119.8, 119.6, 119.3, 105.9, 101.7, 25.1, 13.1. HRMS (ESI) calcd for $C_{20}H_{20}N_3$ $[M+H]^+$: 302.1652, Found: 302.1650.

3-(2,2-Dimethyl-5-phenyl-2H-imidazol-4-yl)-2-phenyl-1H-indole (4c): White solid, yield: 50%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (s, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.26–7.12 (m, 9H), 7.10–7.03 (m, 3H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.4, 160.0, 137.9, 136.2, 132.2, 131.8, 129.5, 128.4, 127.9(127.92), 127.9(127.87), 127.8, 127.6, 127.3, 122.5, 120.2, 119.3, 111.7, 105.6, 101.7, 24.2. HRMS (ESI) calcd for $C_{25}H_{22}N_3$ $[M+H]^+$: 364.1808, Found: 364.1809.

5-Chloro-3-(2,2-dimethyl-5-phenyl-2H-imidazol-4-yl)-2-phenyl-1H-indole (4d): White solid, yield: 74%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.05 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.44 (s, 1H), 7.21 (m, 7H), 7.08 m, 4H), 1.62 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.2, 159.4, 139.8, 134.7, 132.2, 131.4, 129.4, 128.9, 128.5, 128.3, 127.8, 127.7, 127.2, 124.8, 122.5, 118.4, 113.4, 105.2, 101.9, 24.2. HRMS (ESI) calcd for $C_{25}H_{21}N_3Cl$ $[M+H]^+$: 398.1419, Found: 398.1415.

5-Bromo-3-(2,2-dimethyl-5-phenyl-2H-imidazol-4-yl)-1H-indole (4e): White solid, yield: 68%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.63 (s, 1H), 8.42 (d, *J* = 2.0 Hz, 1H), 7.61–7.49 (m, 5H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.33 (m, 1H), 6.95 (s, 1H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 157.7, 134.8, 134.3, 129.8, 129.7, 128.4, 128.3, 128.2, 125.3, 124.0, 114.0, 113.4, 107.5, 101.6, 24.7. HRMS (ESI) calcd for $C_{19}H_{17}N_3Br$ $[M+H]^+$: 366.0600, Found: 366.0601.

6-Fluoro-3-(2,2-dimethyl-5-phenyl-2H-imidazol-4-yl)-1H-indole (4f): White solid, yield: 62%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (s, 1H), 8.28 (dd, *J* = 8.8, 5.7 Hz, 1H), 7.54 (m, 5H), 7.25 (m, 1H), 7.04 (m, 1H), 6.92 (d, *J* = 2.8 Hz, 1H), 1.55 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.8, 159.6 (d, *J* = 236.5 Hz), 136.3 (d, *J* = 12.7 Hz), 134.6, 129.9, 129.3, 128.6, 128.5, 123.3 (d, *J* = 3.7 Hz), 123.2, 109.4, 109.1, 108.2, 101.6, 98.2 (d, *J* = 25.1 Hz), 24.9. HRMS (ESI) calcd for $C_{19}H_{17}FN_3$ $[M+H]^+$: 306.1401 , Found: 306.1398.

5-Methoxy-3-(2,2-dimethyl-5-phenyl-2H-imidazol-4-yl)-1H-indole (4g): White solid, yield: 50%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 1H), 7.78 (d, *J* = 2.5 Hz, 1H), 7.59–7.49 (m, 5H), 7.35 (d, *J* = 8.8 Hz, 1H), 6.90–6.84 (m, 2H), 3.76 (s, 3H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.0, 158.3, 154.8, 134.8, 131.3, 129.8, 129.1, 128.5(128.54), 128.5(128.49), 127.2, 112.7, 112.6, 107.9, 104.3, 101.5, 55.6, 25.1. HRMS (ESI) calcd for $C_{20}H_{20}N_3O$ $[M+H]^+$: 318.1601, Found: 318.1601.

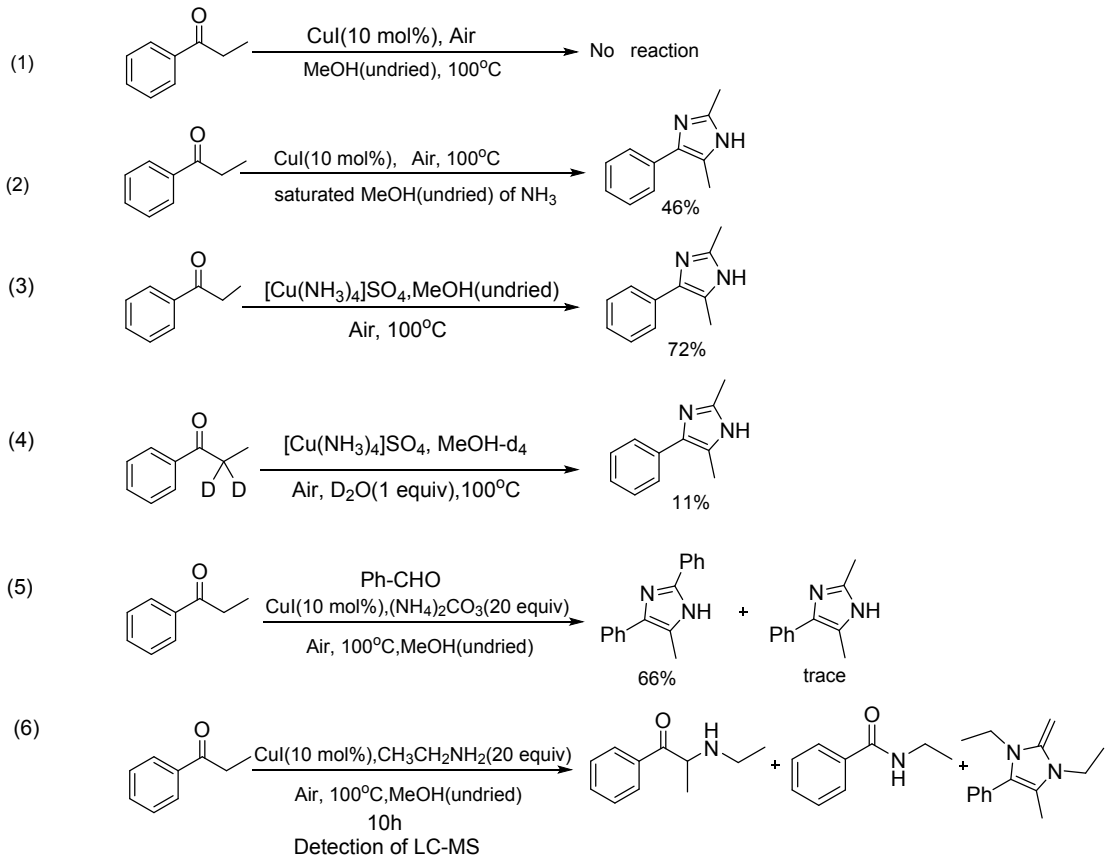
5-Chloro-3-(2,2-dimethyl-5-(p-Tolyl)-2H-imidazol-4-yl)-2-phenyl-1H-indole (4h): White solid, yield: 55%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.07 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.23 (m, 6H), 7.06 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 2.15 (s, 3H), 1.60 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.2, 159.8, 139.7, 139.3, 134.9, 131.6, 129.5, 129.2, 128.6(128.56), 128.6(128.56), 128.4, 127.9, 127.5, 125.0, 122.6, 118.5, 113.5, 105.6, 101.9, 24.4, 21.0. HRMS (ESI) calcd for $C_{26}H_{23}ClN_3$ $[M+H]^+$: 412.1575, Found: 412.1475.

3-(2,2-Dimethyl-5-(p-tolyl)-2H-imidazol-4-yl)-2-methyl-1H-indole (4i): White solid, yield: 50%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.39 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.9 Hz,1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.08–7.00 (m, 2H), 6.84 (m, 1H), 2.29 (s, 3H), 2.10 (s, 3H), 1.54 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.0, 159.7, 139.9, 137.0, 135.4, 130.4, 129.1, 128.2, 127.3, 121.2, 119.6, 119.3, 111.1, 105.6, 101.3, 25.0, 21.2, 12.9. HRMS (ESI) calcd for $C_{21}H_{22}N_3$ $[M+H]^+$: 316.1807, Found: 316.1805.

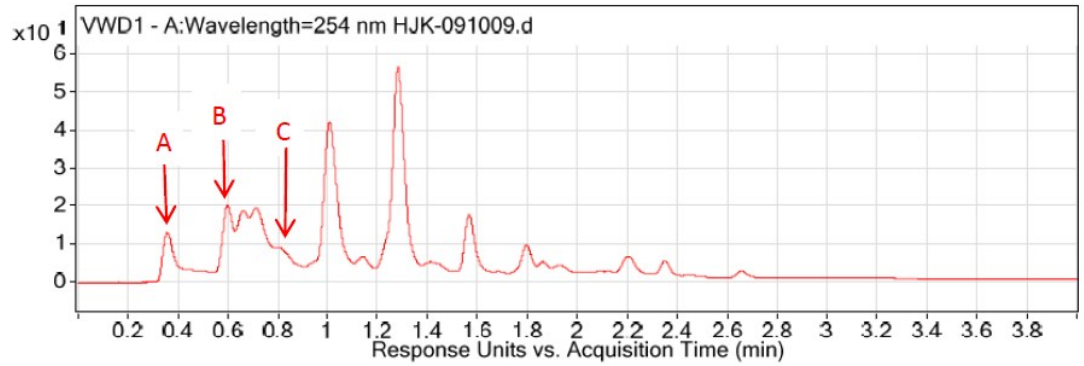
3-(2-Ethyl-5-phenyl-2-(p-Tolyl)-2H-imidazol-4-yl)-2-methyl-1H-indole (4j): White solid, yield: 52%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.50 (s, 1H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.59–7.53 (m, 2H), 7.48–7.42 (m, 1H), 7.39–7.32 (m, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.09–7.02 (m, 2H), 6.86 (t, *J* = 7.5 Hz, 1H), 2.30 (s, 3H), 2.28–2.21 (m, 2H), 2.13 (s, 3H), 0.75 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.3, 160.4, 138.3, 137.3, 136.4, 135.3, 133.0, 130.1, 128.7, 128.5, 128.1, 127.3, 127.2, 121.1, 119.5, 119.0, 111.0, 107.2, 105.3, 34.0, 20.7, 12.7, 8.4. HRMS (ESI) calcd for $C_{27}H_{26}N_3$ $[M+H]^+$: 392.2127 , Found: 392. 2197.

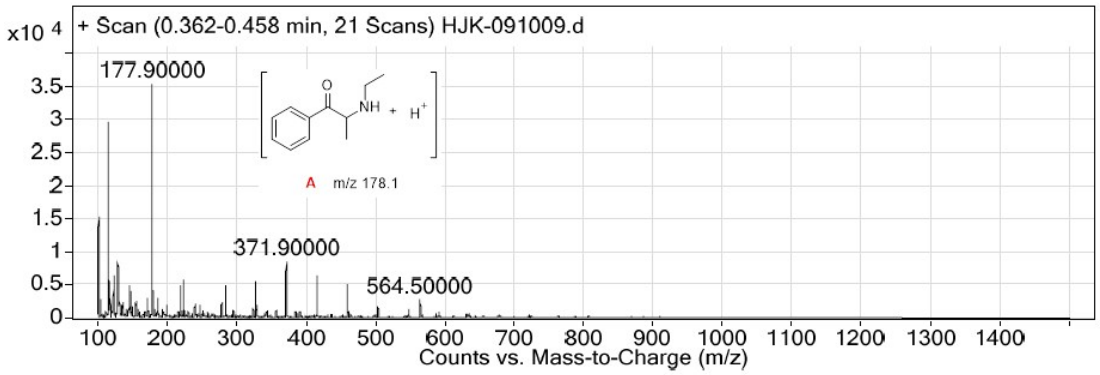
6. Mechanistic study

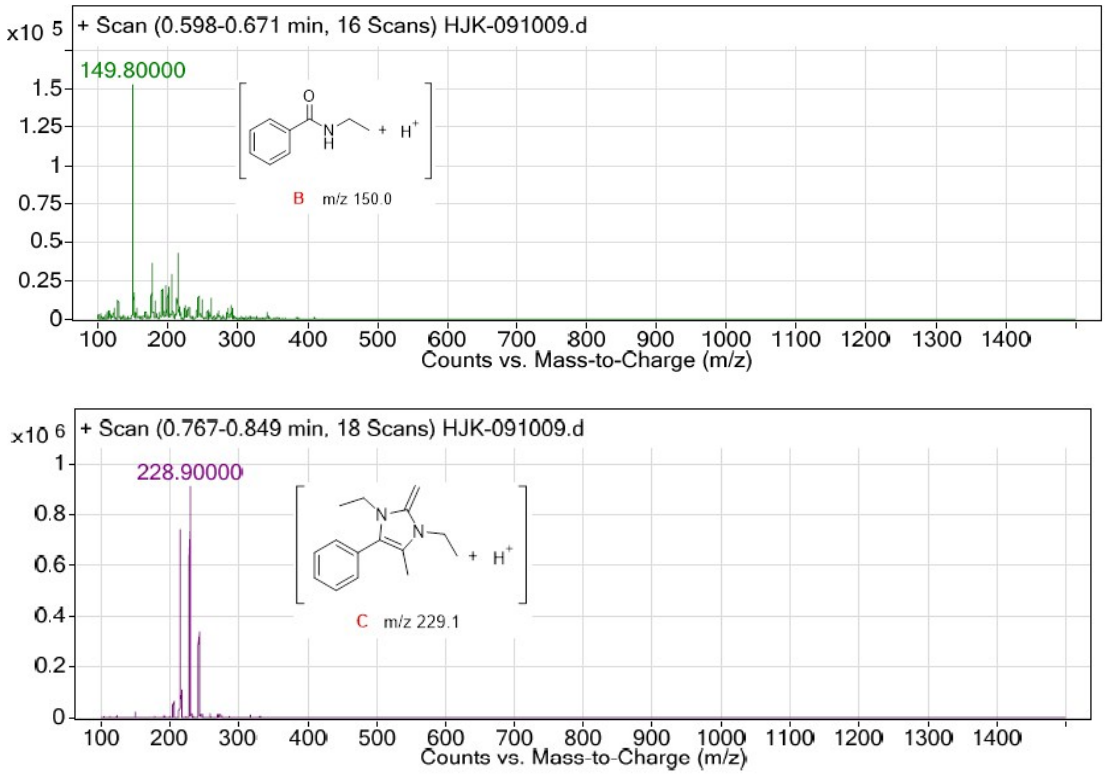
6.1 Exploration of reaction process



Detection of LC-MS of reaction 6







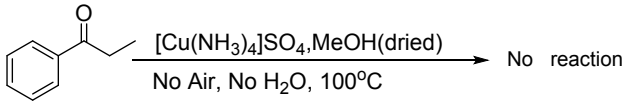
To understand the reaction for novel imidazole synthesis well, we designed a series of experiments to observe the special effects of some conditions on the imidazole synthesis. The effect of the nitrogen source on the reaction was first investigated. As shown in **reaction 1**, no reaction occurred in the absence of $(NH_4)_2CO_3$.This result indicates that $(NH_4)_2CO_3$ is really a nitrogen source for the reaction and it may decompose into ammonia to form a complex with copper and participates in the catalytic cycle. To confirm this point, ammonia-saturated methanol was used as the reaction solvent (**reaction 2**). The reaction occurred, but the yield of the corresponding product was only 46%. This lower yield may be due to the fact that only a limited amount of ammonia dissolved in methanol. Subsequently, the copper-ammonia complex was prepared by the reaction of the copper salt with excess ammonia water and was used in the reaction 3a. The result shows that the product was obtained in 72% yield, which confirmed that the copper-ammonia complex was not only the catalyst of the reaction, but also the nitrogen source. In addition, the effects of air and water on the reaction were also investigated (**reactions 3**). In the absence of water(anhydrous methanol) or air, no target product was obtained, indicating that water and air are necessary for the reaction. It is suggested that the breaking of C-C bond of propiophenone may be realized by the joint involving of oxygen and water. Further, to confirm the α-C-H activation and α-amination in the imidazole formation, α-perdeuterated propiophenone was used as the substrate using deuterated methanol as solvent in the presence of dry air and D_2O, the product was obtained in only 11% yield (**reaction 4**). The results show that C-H activation is a prerequisite for the reaction process.

Referring to the C-C bond cleavage reaction [11, 15], during the formation of imidazoles, we speculated that a portion of propiophenone may undergo cleavage of the C-C bond to produce an aldehyde. In order to confirm this, benzaldehyde was added to the reaction system, and only trace amount of original product **2a** was found. In contrast, the corresponding aldehyde condensation products was obtained in yields of 66% , respectively (**reactions 5**). If 4 equivalents of benzaldehyde are added, the formation of

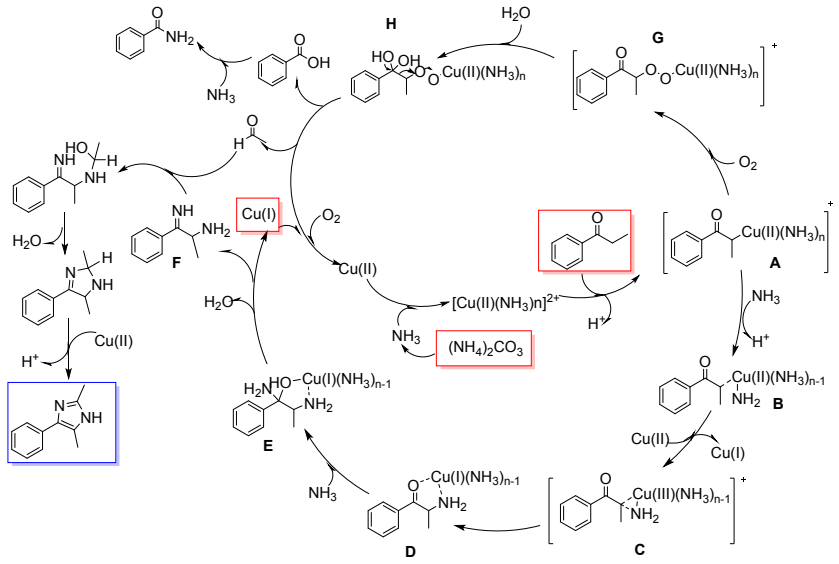
2a can also be completely inhibited. The results indicate that a competitive reaction occurs when an excess of other aldehyde is present, and the root cause is related to the thermodynamic and kinetic differences in the cleavage of the old bond and the formation of the new bond during the reaction.

At the same time, ethylamine was used as a nitrogen source and phenylacetone as a substrate to react under the same reaction conditions. The intermediates *α*-ethylpheny-lacetone, (E)-ethylacetone-1-(ethylimino)-1-phenyl-propan-2-amine and *N*-ethylbenzamide and their products 1,3-diethyl-4- methyl-ene-5-phenyl-2,3-dihydro1-himidazole were found by LC-MS(**reaction 6**).

In addition, the effects of air and water on the reaction were also tested(As follows). In the absence of water(anhydrous methanol) or air, no corresponding target product was obtained.

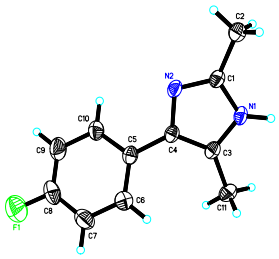


6.2 A proposed reaction pathway for imidazole synthesis



7. Crystal data

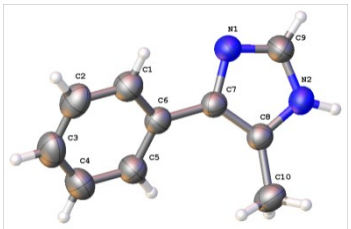
7.1 Crystal data of 4-(4-fluorophenyl)-2,5-dimethyl-1*H*-imidazole(CCDC 1853653)



Empirical formula	$C_{11}H_{11}FN_2$	
Formula weight	180.72	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	I b a 2	
Unit cell dimensions	a = 9.8331(14) Å	α= 90°.
	b = 20.335(3) Å	β= 90°.
	c = 9.8331(14) Å	γ= 90°.
Volume	1966.2(5) $Å^3$	
Z	8	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	764	
Crystal size	0.211 x 0.102 x 0.056 mm^3	
Theta range for data collection	2.003 to 25.997°.	
Index ranges	$-8\leq h\leq 12$, $-24\leq k\leq 24$, $-12\leq l\leq 12$	
Reflections collected	5677	
Independent reflections	1892 [R(int) = 0.0368]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6452	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1892 / 1 / 133	
Goodness-of-fit on F^2	1.197	
Final R indices [I>2sigma(I)]	R1 = 0.0544, wR2 = 0.1250	

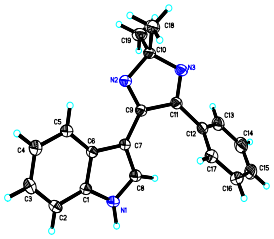
R indices (all data)	R1 = 0.0596, wR2 = 0.1283
Absolute structure parameter	1.5(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.193 and -0.138 e.Å^{-3}

7.2 Crystal data of5-methyl-4-phenyl-1*H*-imidazole(CCDC 1882199)



Empirical formula	$C_{10}H_{10}N_2$	
Formula weight	158.20	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 9.612(3) Å	α= 90°.
	b = 7.441(2) Å	β= 90°.
	c = 24.001(7) Å	γ= 90°.
Volume	1716.6(9) Å^3	
Z	8	
Density (calculated)	1.224 Mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	672	
Crystal size	0.12 x 0.1 x 0.05 mm^3	
Theta range for data collection	1.697 to 27.497°.	

Index ranges	-12≤h≤12, -9≤k≤9, -24≤l≤31
Reflections collected	12822
Independent reflections	1974 [R(int) = 0.0580]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6851
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1974 / 0 / 110
Goodness-of-fit on F^2	1.103
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1100
R indices (all data)	R1 = 0.1112, wR2 = 0.1333
Extinction coefficient	n/a
Largest diff. peak and hole	0.125 and -0.217 e.$Å^{-3}$

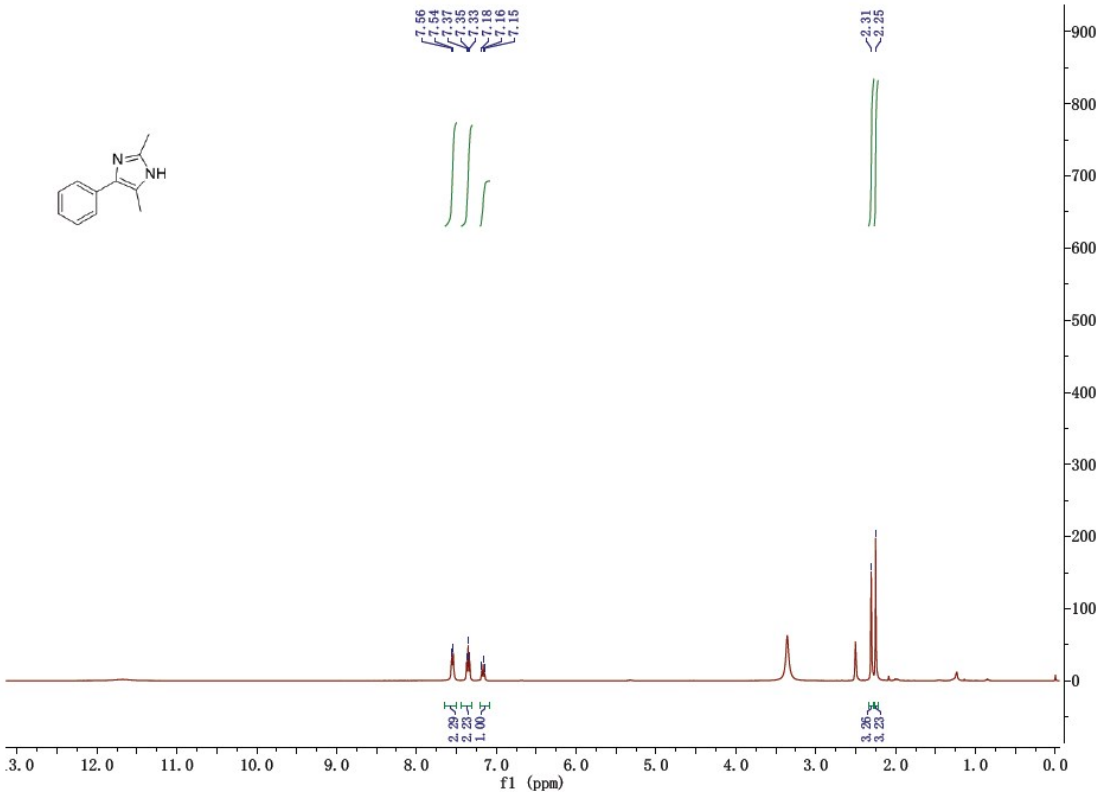


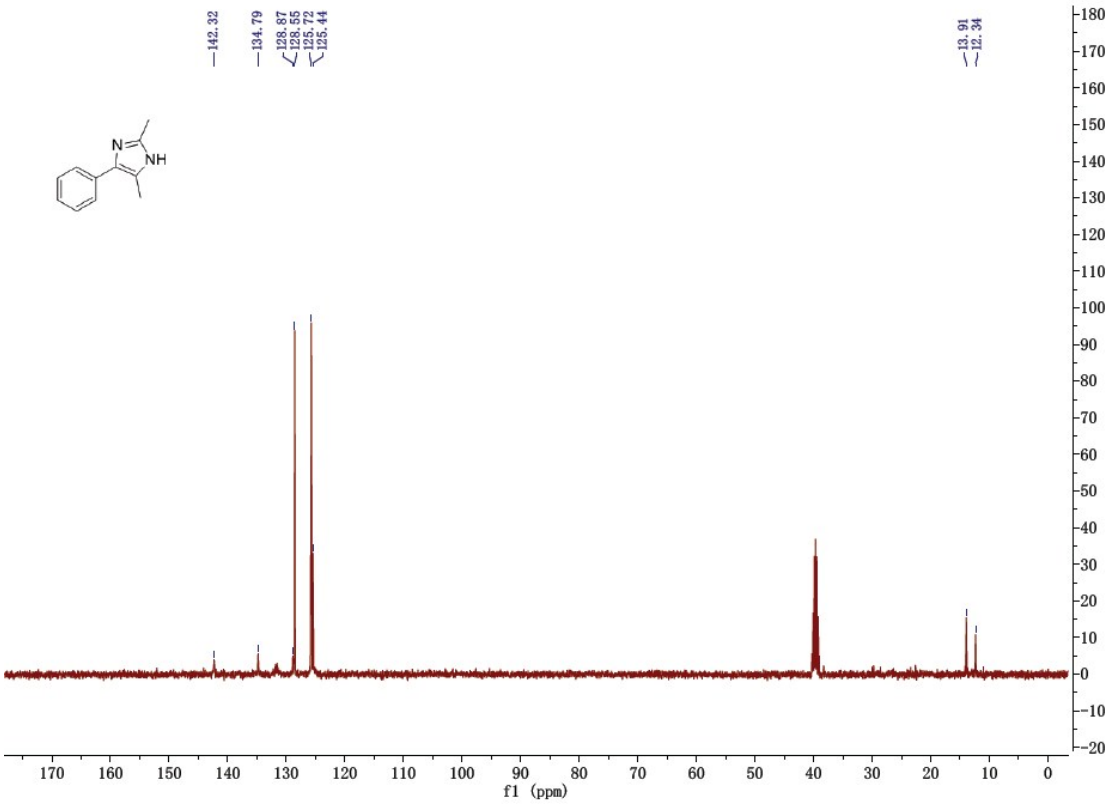
7.3 Crystal data of 3-(2,2-dimethyl-5-phenyl-2H-imidazol-4-yl)-1H-indole(CCDC 1882198)

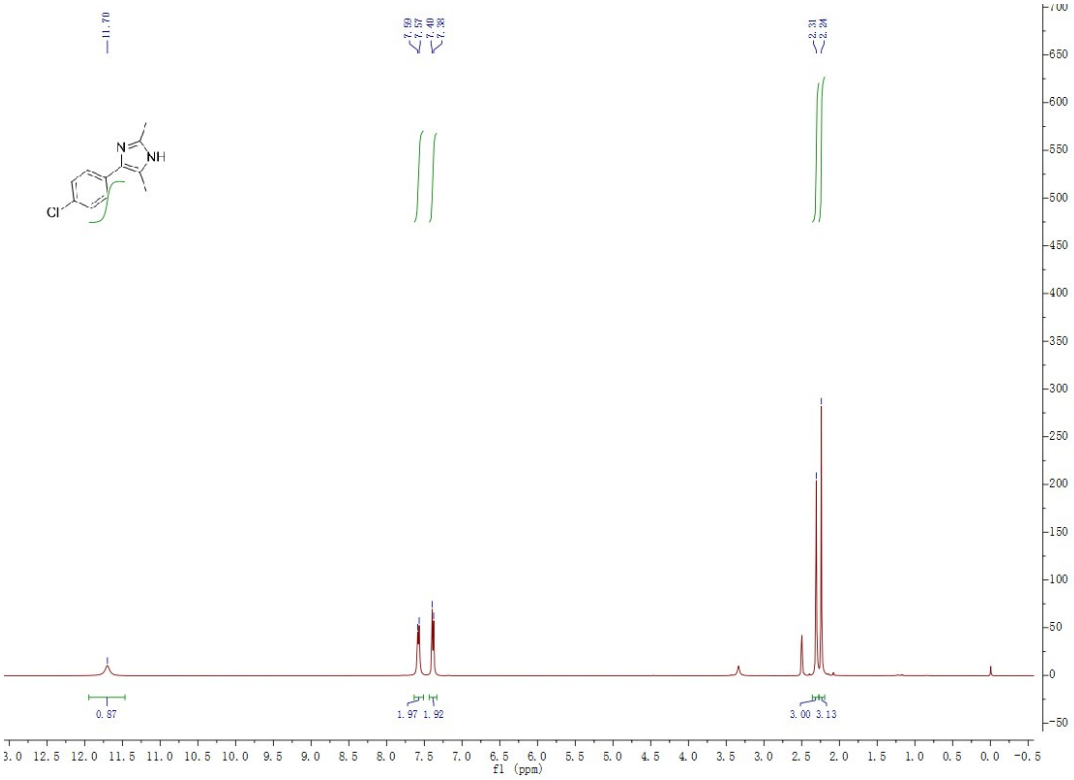
Empirical formula	$C_{19}H_{17}N_3$	
Formula weight	287.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.8979(10) Å	α= 90°.

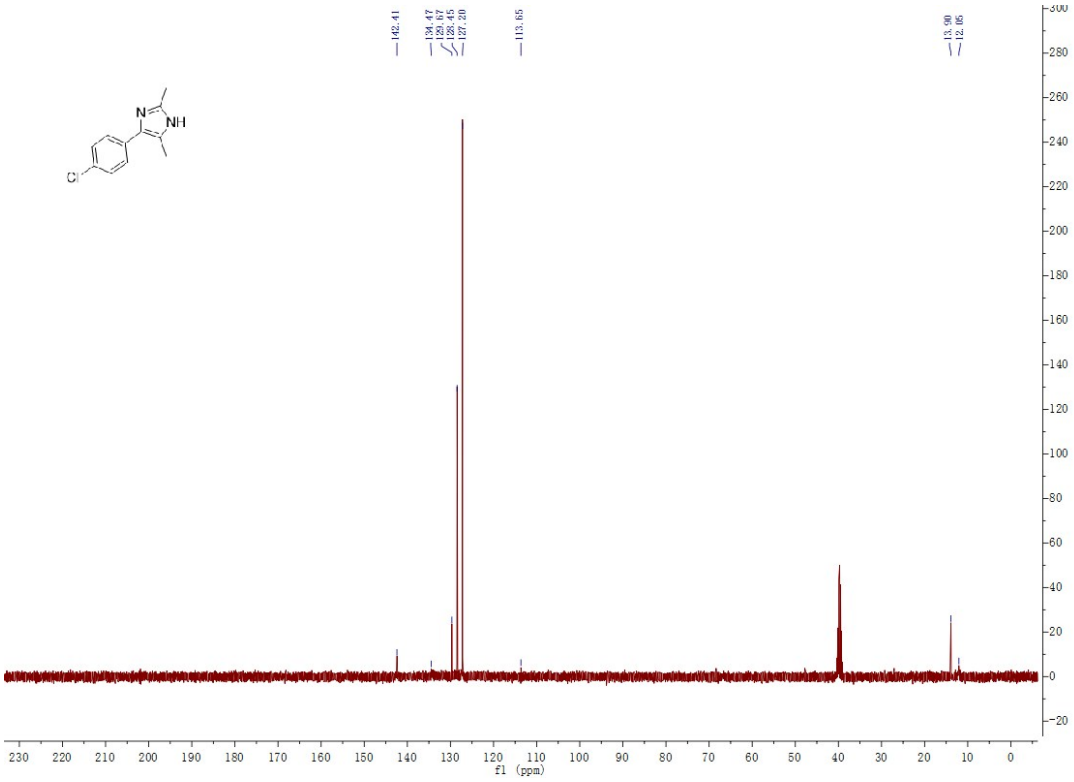
	b = 16.1189(18) Å β= 98.182(3)°.
	c = 10.7902(12) Å γ= 90°.
Volume	1531.8(3) $Å^3$
Z	4
Density (calculated)	1.246 Mg/m^3
Absorption coefficient	0.075 mm^{-1}
F(000)	608
Crystal size	0.180 x 0.130 x 0.080 mm^3
Theta range for data collection	2.288 to 25.996°.
Index ranges	-10≤h≤10, -19≤k≤19, -9≤l≤13
Reflections collected	9181
Independent reflections	3004 [R(int) = 0.0397]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6486
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3004 / 0 / 206
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0511, wR2 = 0.1135
R indices (all data)	R1 = 0.0787, wR2 = 0.1279
Extinction coefficient	0.0055(12)
Largest diff. peak and hole	0.183 and -0.162 $e.Å^{-3}$

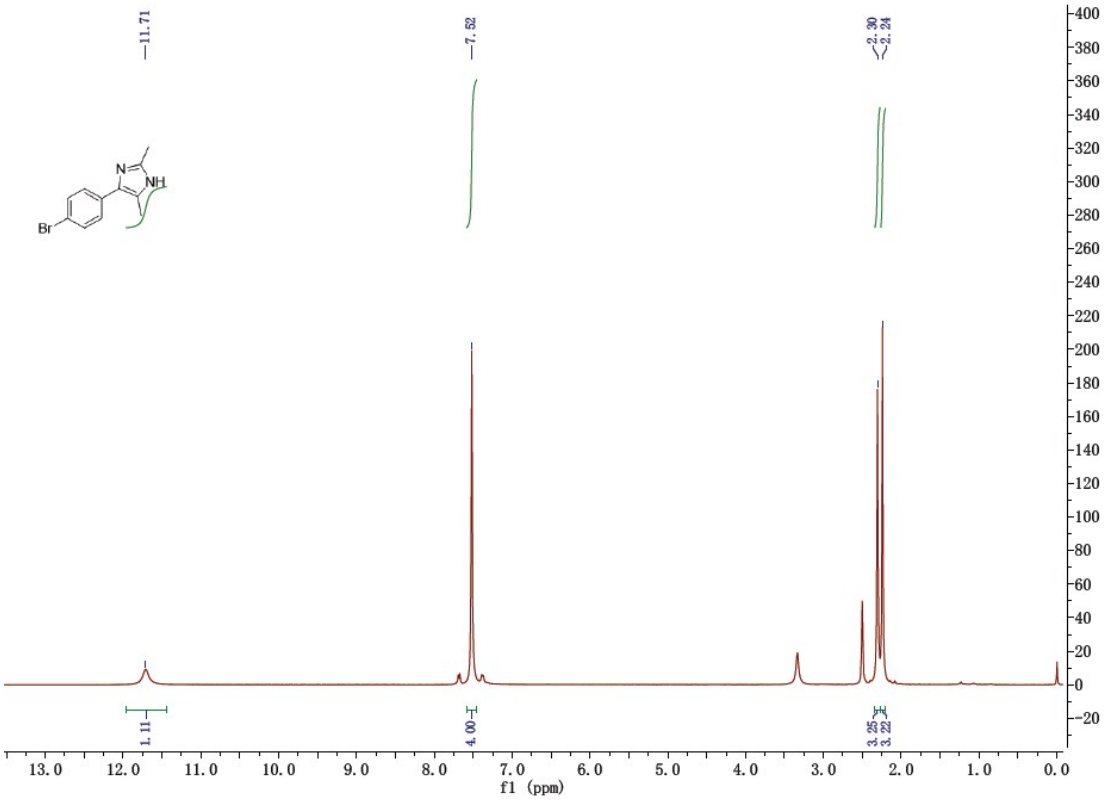
8. NMR spectra

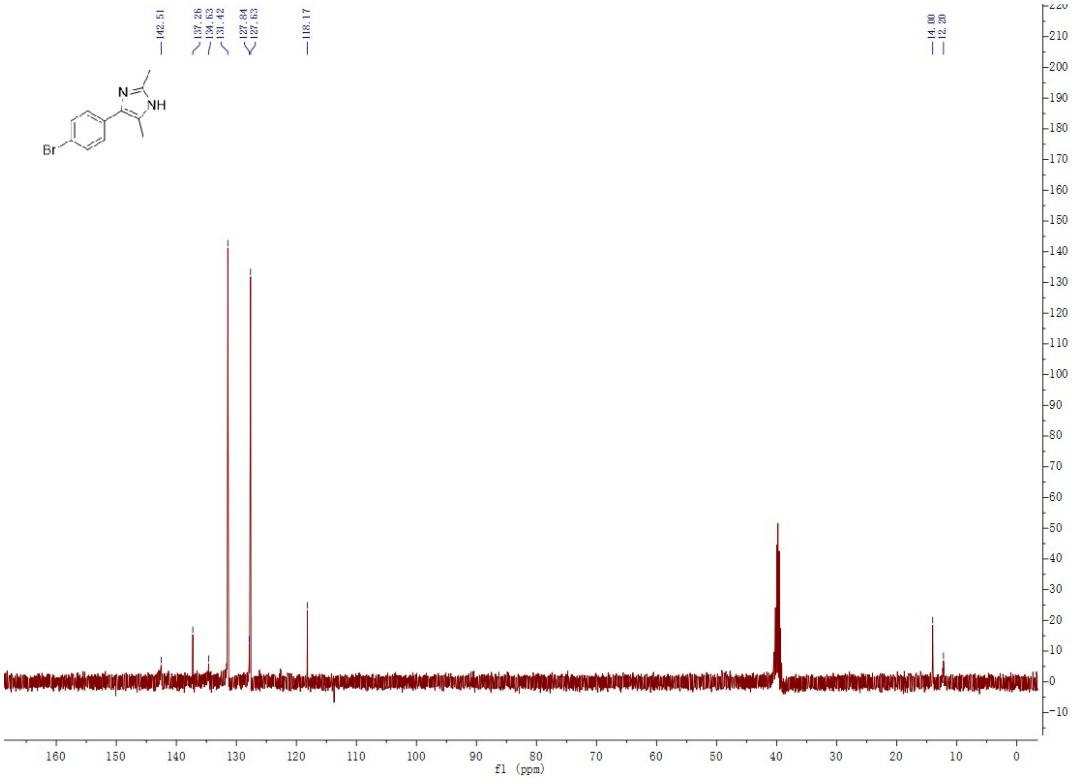


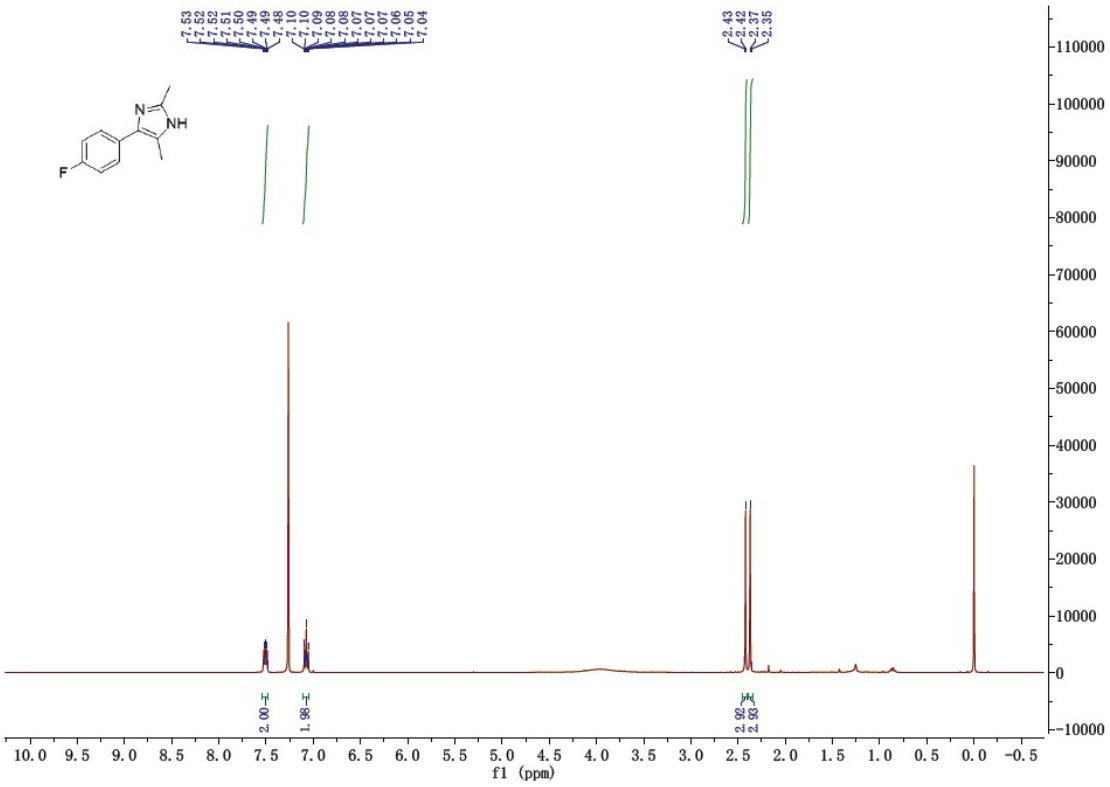

142.32
134.79
128.87
128.65
125.72
125.44
13.91
12.34
N
NH
f1 (ppm)

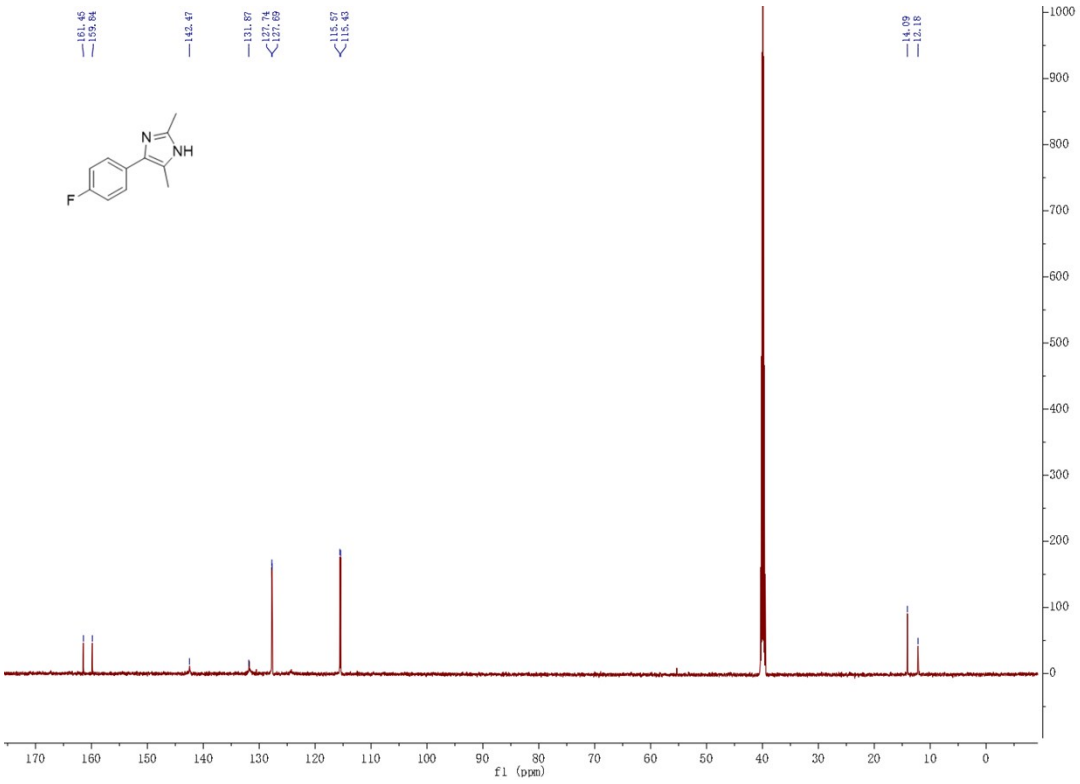

11.70
7.59
7.57
7.40
7.38
2.31
2.24
N
NH
Cl
0.87
1.97
1.92
3.00
3.13
f1 (ppm)

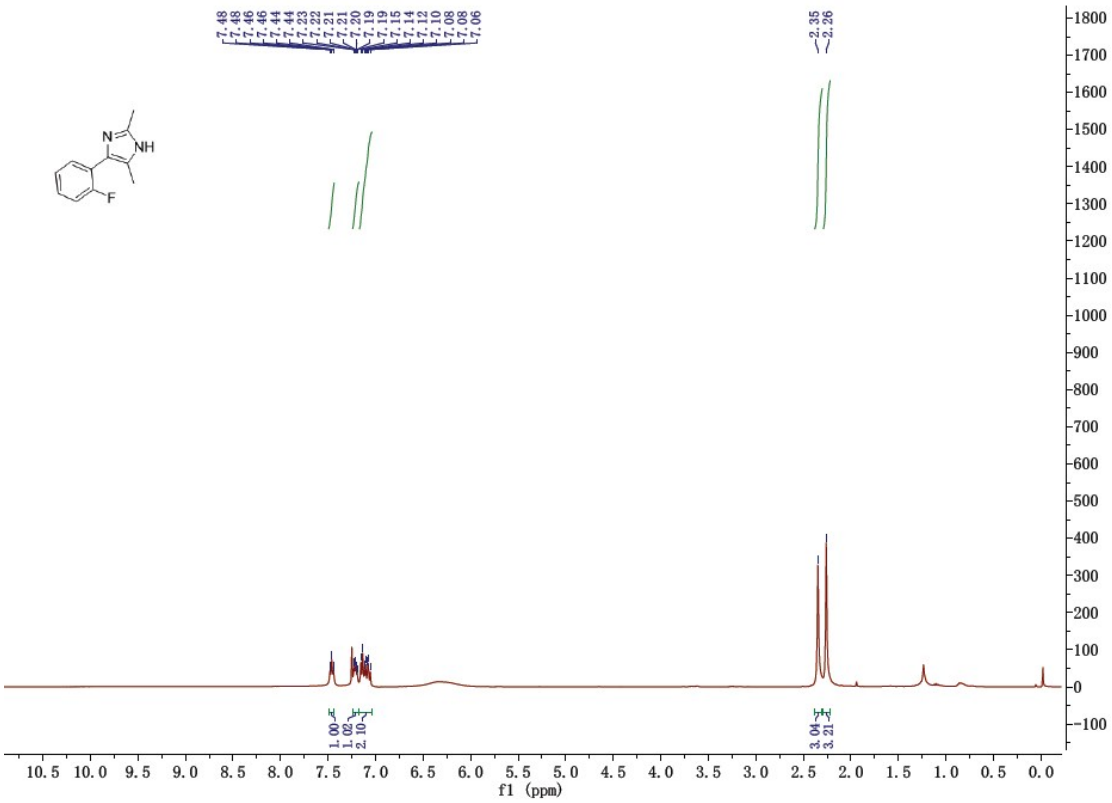

142.41
134.47
129.67
128.45
127.20
113.65
13.90
12.05
N
NH
Cl
f1 (ppm)

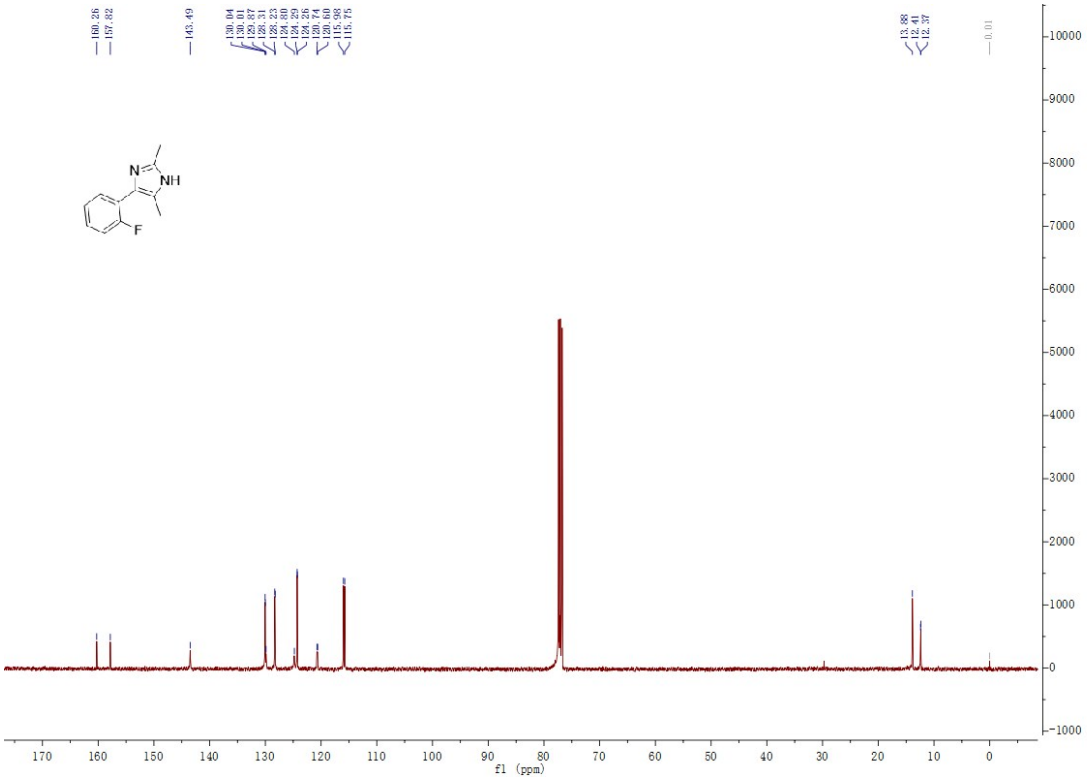

11.71
7.52
2.30
2.24
N
NH
Br
1.11
4.00
3.25
3.22
f1 (ppm)


142.51
137.26
134.63
131.42
127.84
127.63
118.17
14.00
12.20
N
NH
Br
f1 (ppm)


7.53
7.52
7.52
7.51
7.50
7.49
7.49
7.48
7.10
7.09
7.08
7.08
7.07
7.07
7.07
7.06
7.05
7.04
2.43
2.42
2.37
2.35
N
NH
F
2.00
1.98
2.92
2.93
f1 (ppm)


161.45
159.84
142.47
131.87
122.74
127.69
115.57
115.43
14.09
12.18
N
NH
F
f1 (ppm)


7.48
7.48
7.46
7.46
7.44
7.44
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.15
7.14
7.12
7.10
7.08
7.08
7.06
2.35
2.26
N
NH
F
1.00
1.02
2.10
3.04
3.21
f1 (ppm)


160.26
157.82
143.49
130.04
130.01
128.87
128.31
128.23
124.80
124.29
124.26
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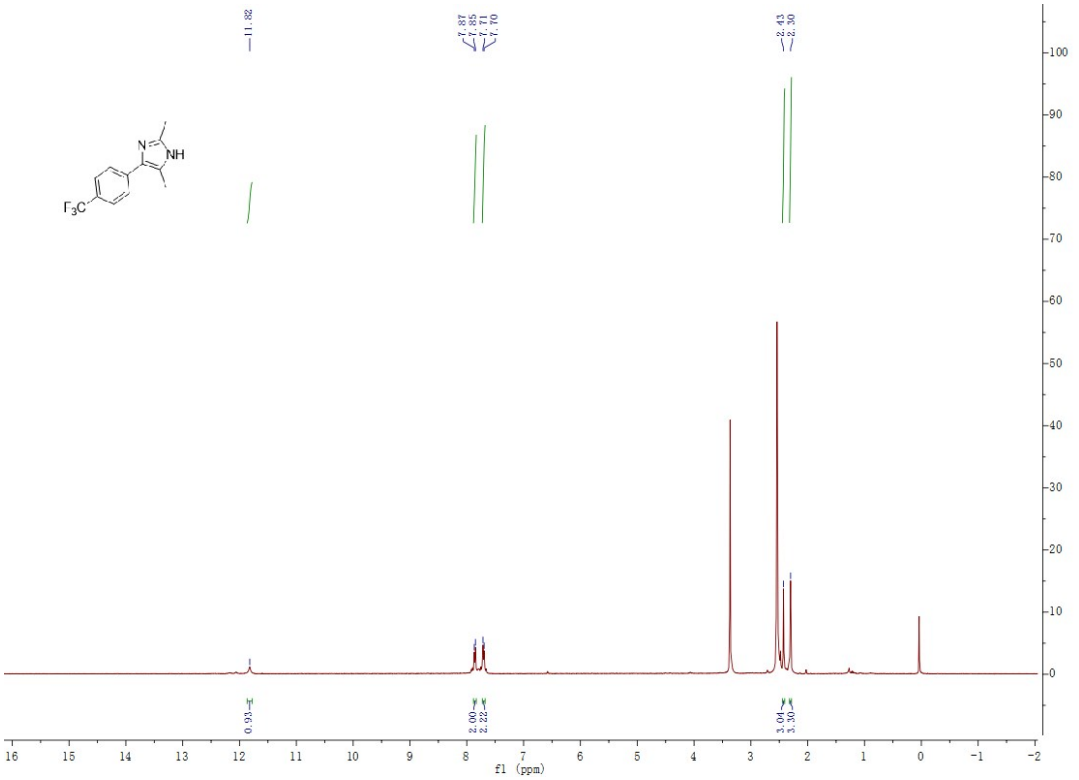
120.60
115.98
115.75
13.88
12.41
12.37
0.01
N
NH
F
f1 (ppm)


11.82
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7.85
7.71
7.70
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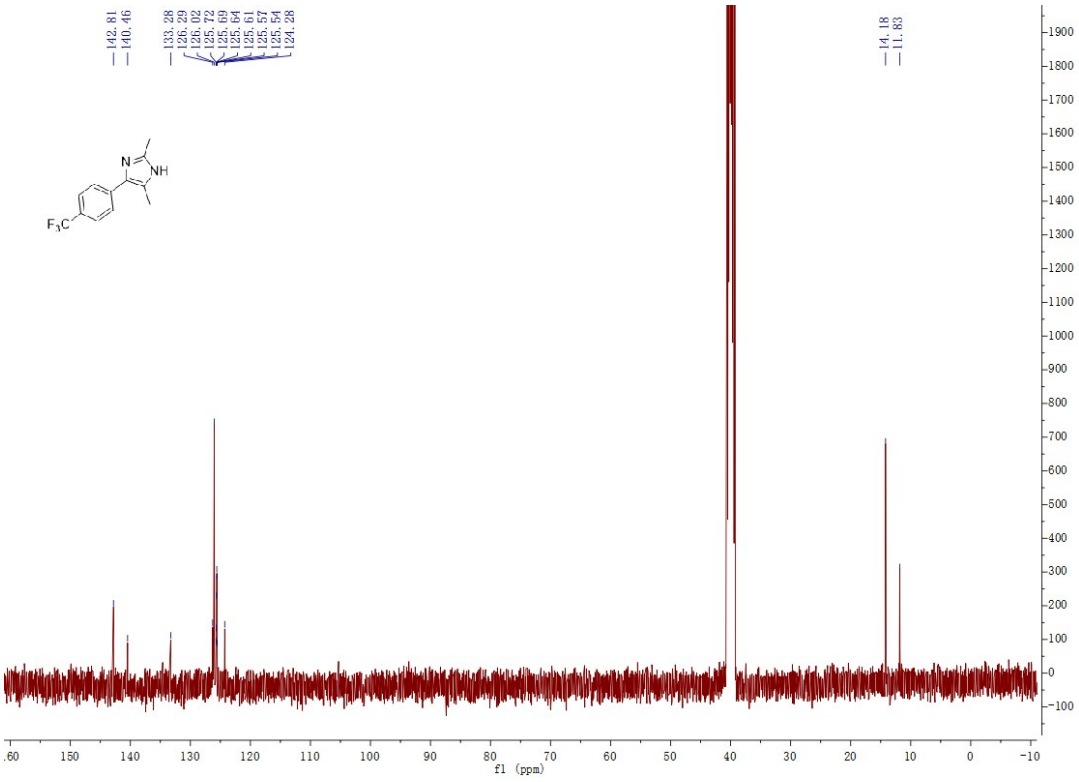
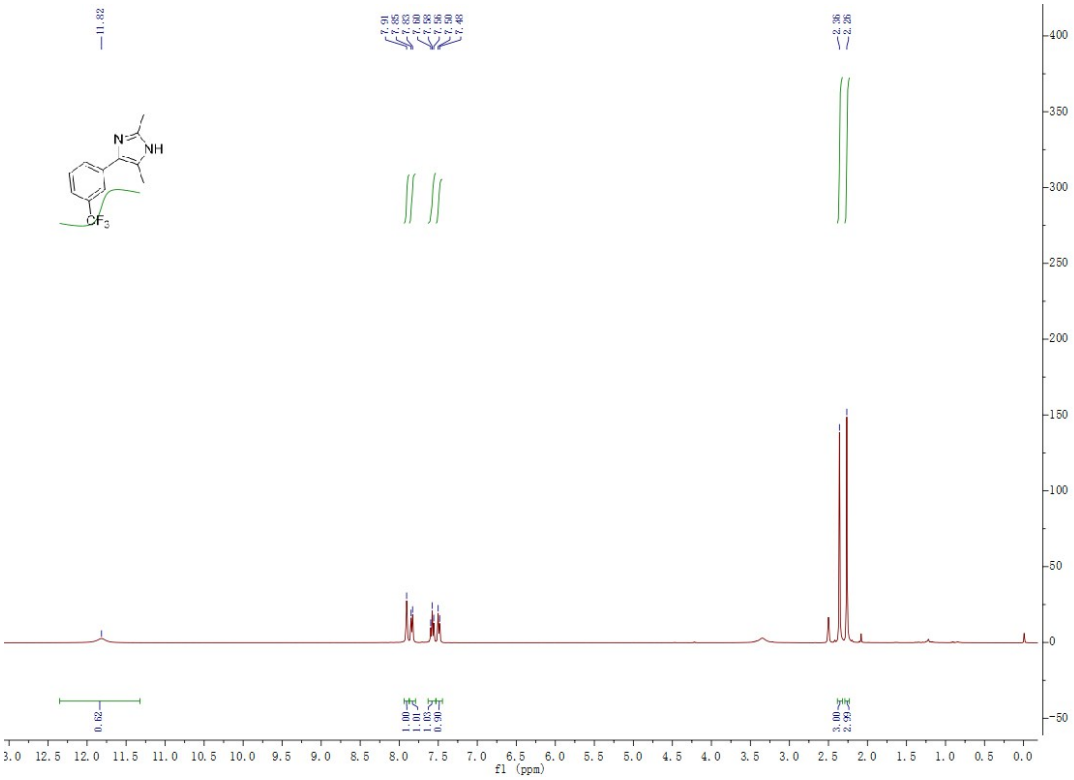
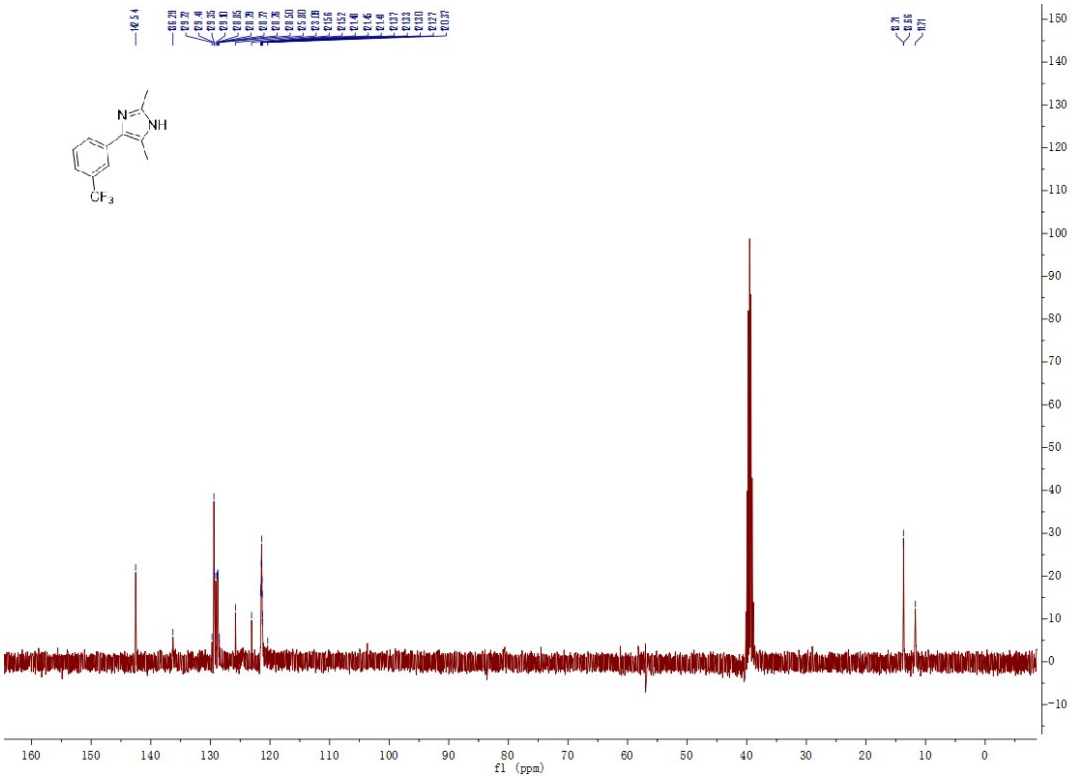
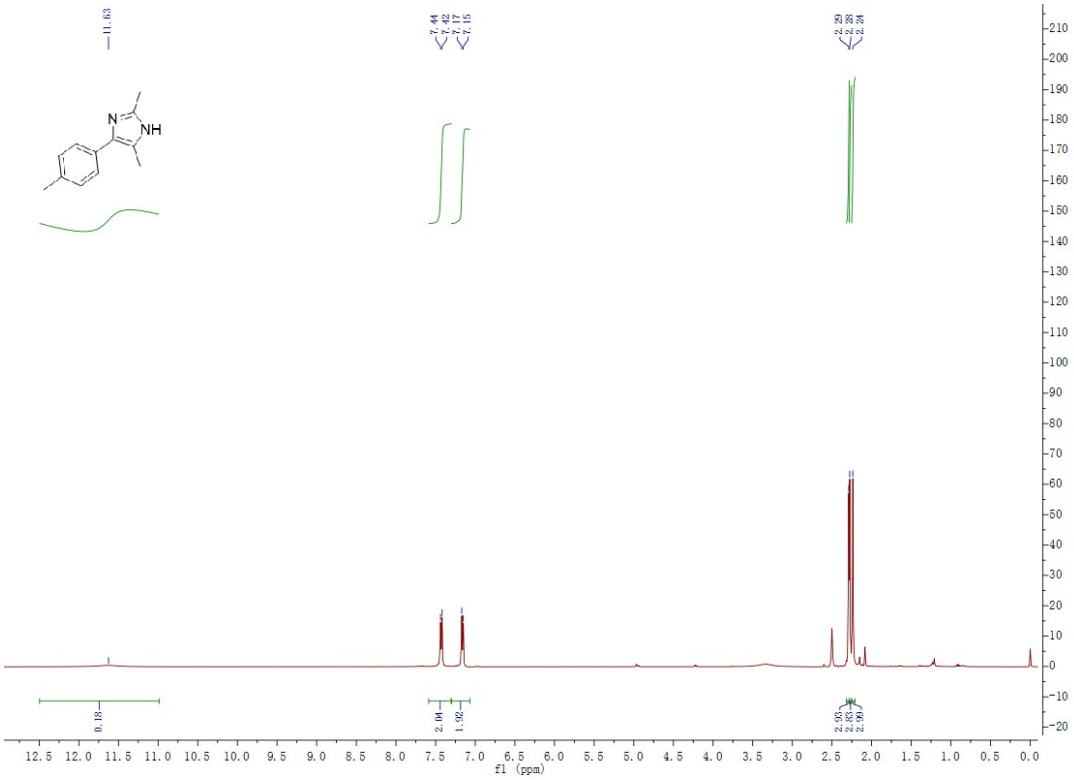
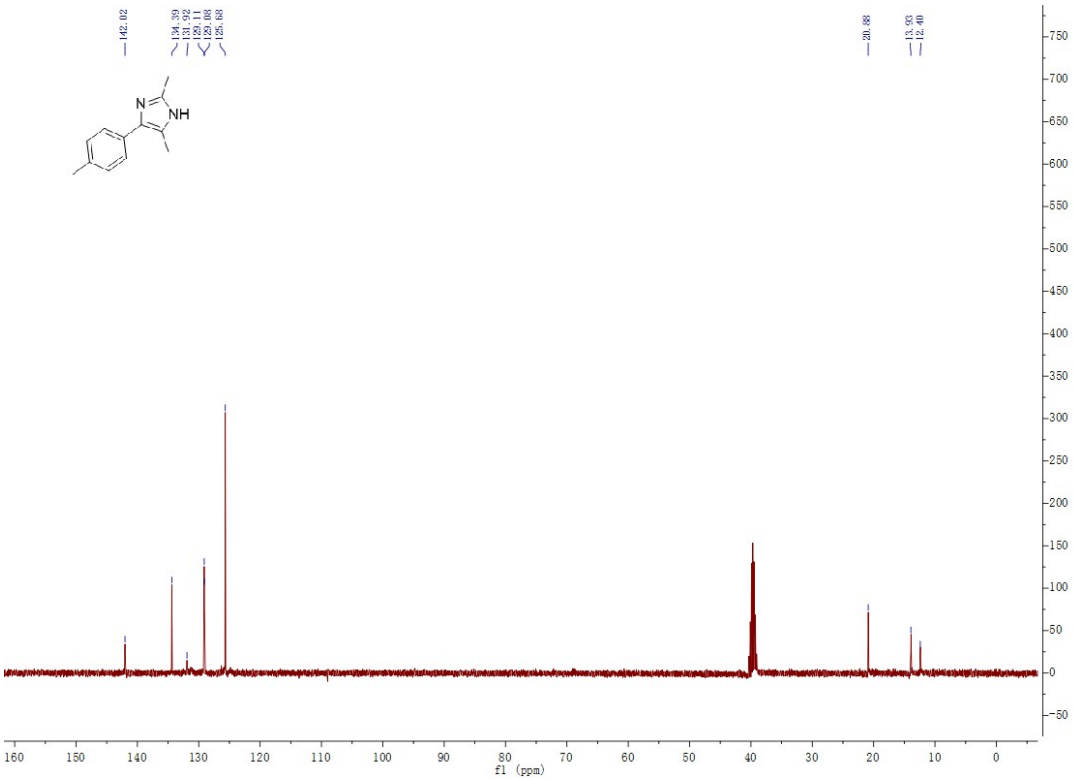
2.30
0.93
2.00
2.22
3.04
3.30
f1 (ppm)

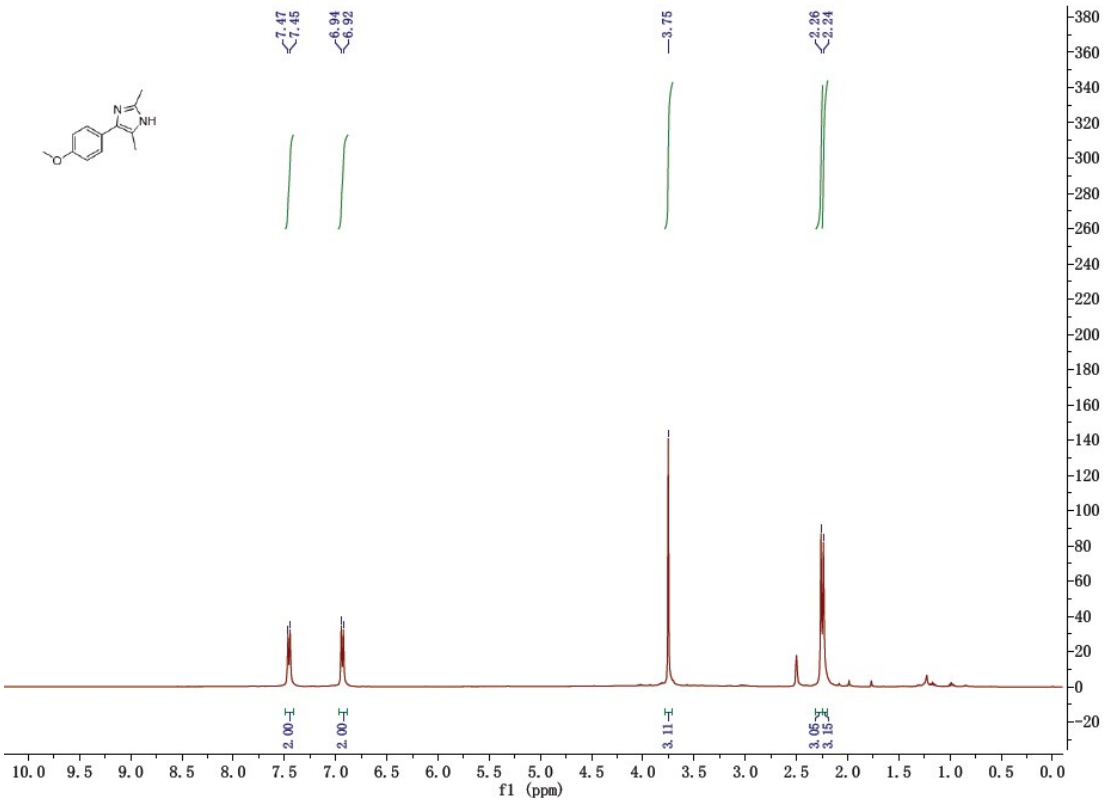

142.81
140.46
133.28
126.29
126.02
125.72
125.69
125.64
125.61
125.57
125.54
124.28
14.18
11.83
f1 (ppm)


11.82
7.91
7.85
7.65
7.60
7.58
7.56
7.50
7.48
2.36
2.25
N
NH
CF3
0.62
1.00
1.01
1.05
0.90
3.00
2.99
f1 (ppm)


140.54
N
NH
CF3
f1 (ppm)


11.63
7.44
7.42
7.17
7.15
2.29
2.26
2.24
N
NH
0.18
2.04
1.92
2.93
2.83
2.90
f1 (ppm)


142.02
134.39
131.92
129.11
128.08
125.68
20.88
13.93
12.40
N
NH
f1 (ppm)


7.47
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6.92
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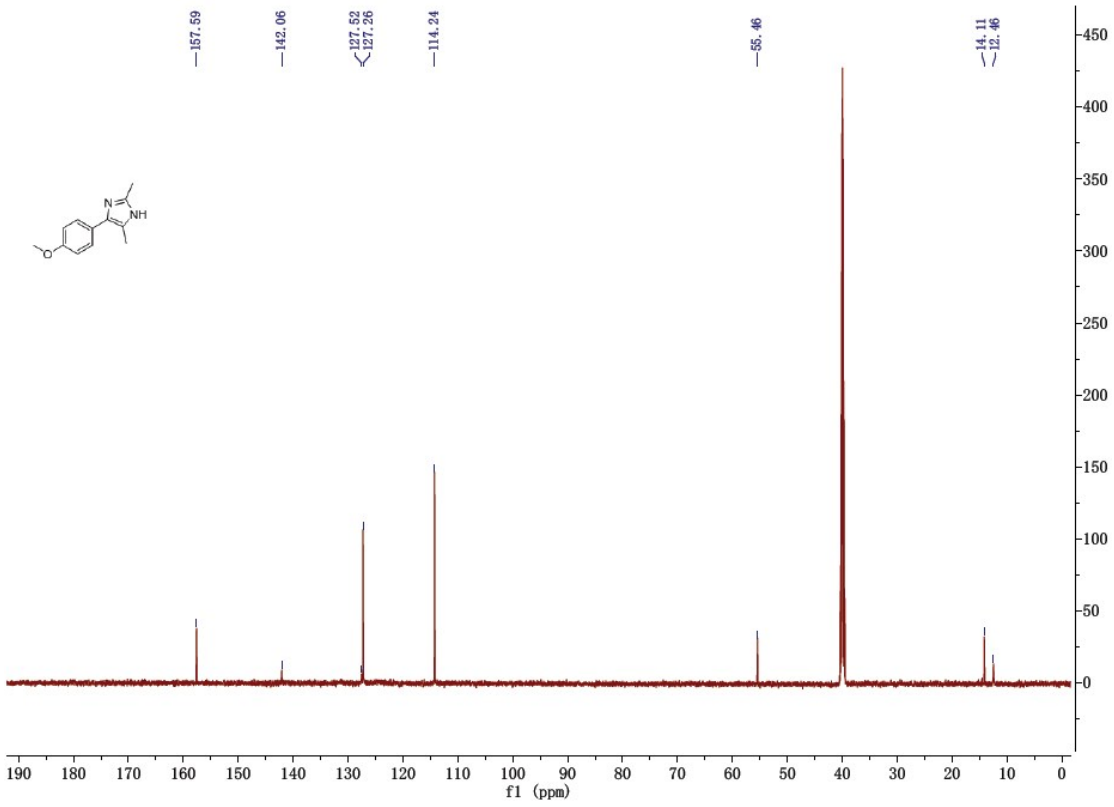
2.26
2.24
2.00
2.00
3.11
3.05
3.15
f1 (ppm)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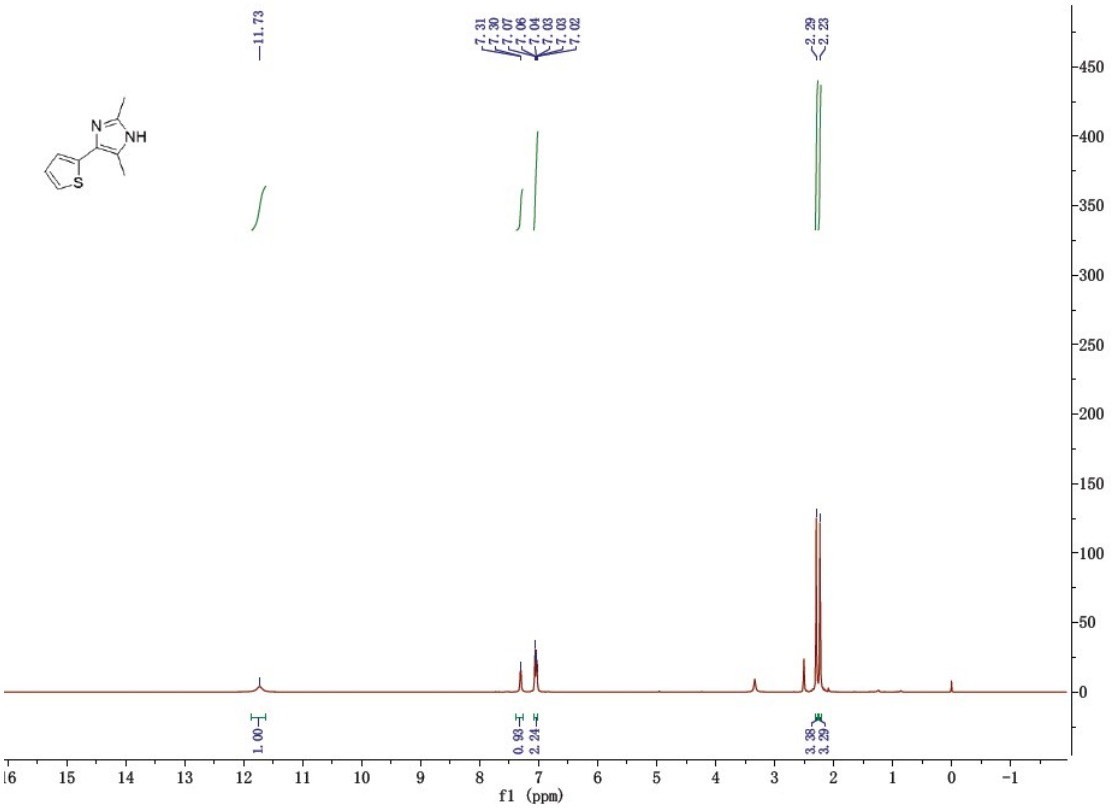
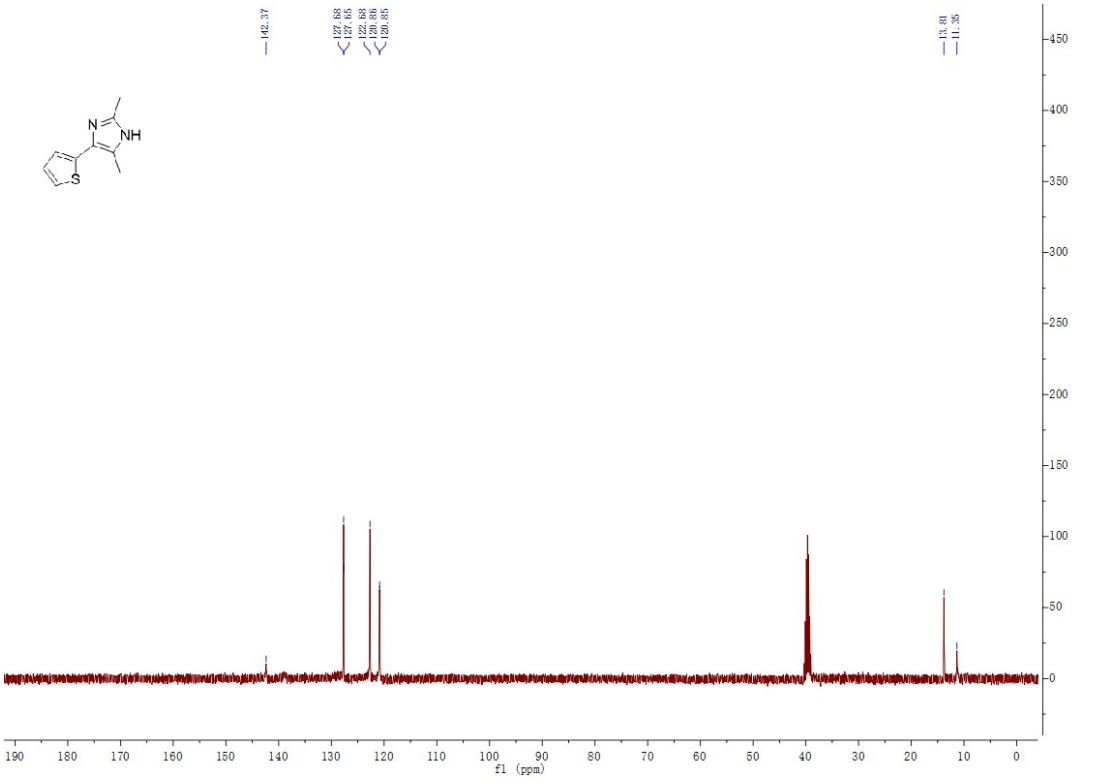
142.06
127.52
127.26
114.24
55.46
14.11
12.46
f1 (ppm)


11.73
7.31
7.30
7.07
7.06
7.04
7.03
7.03
7.02
2.29
2.23
1.00
0.93
2.24
3.38
3.29
f1 (ppm)


142.37
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127.65
122.68
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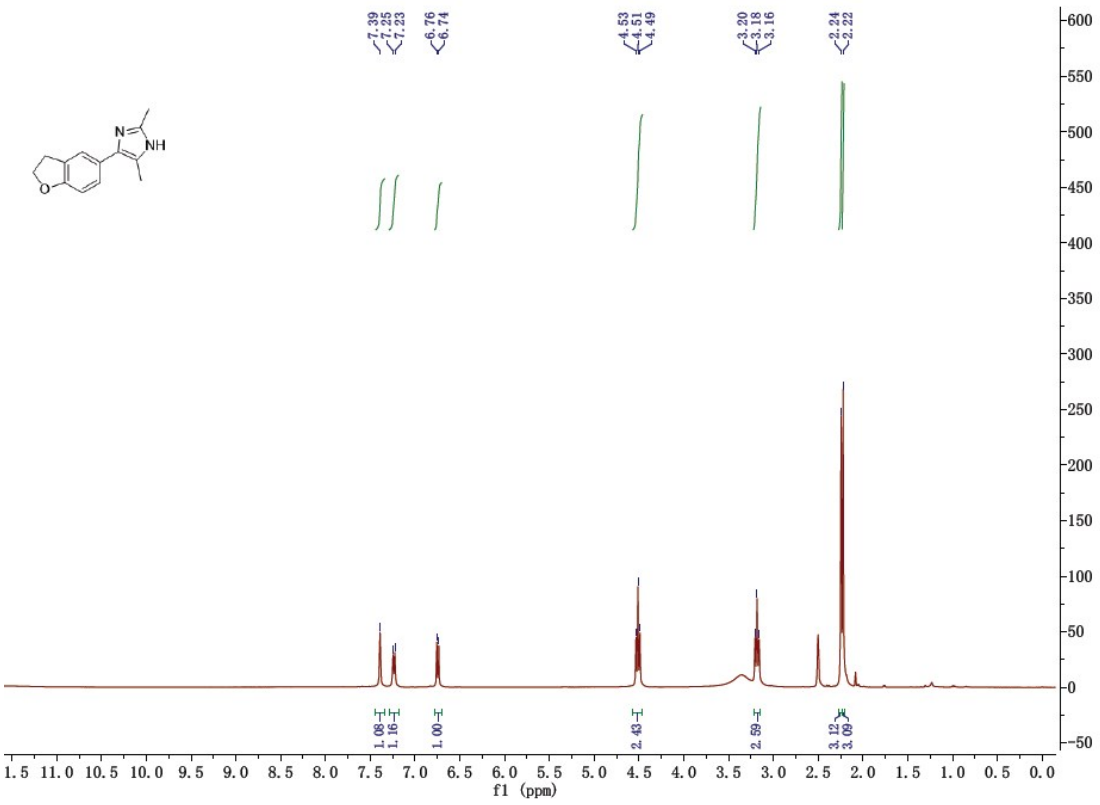
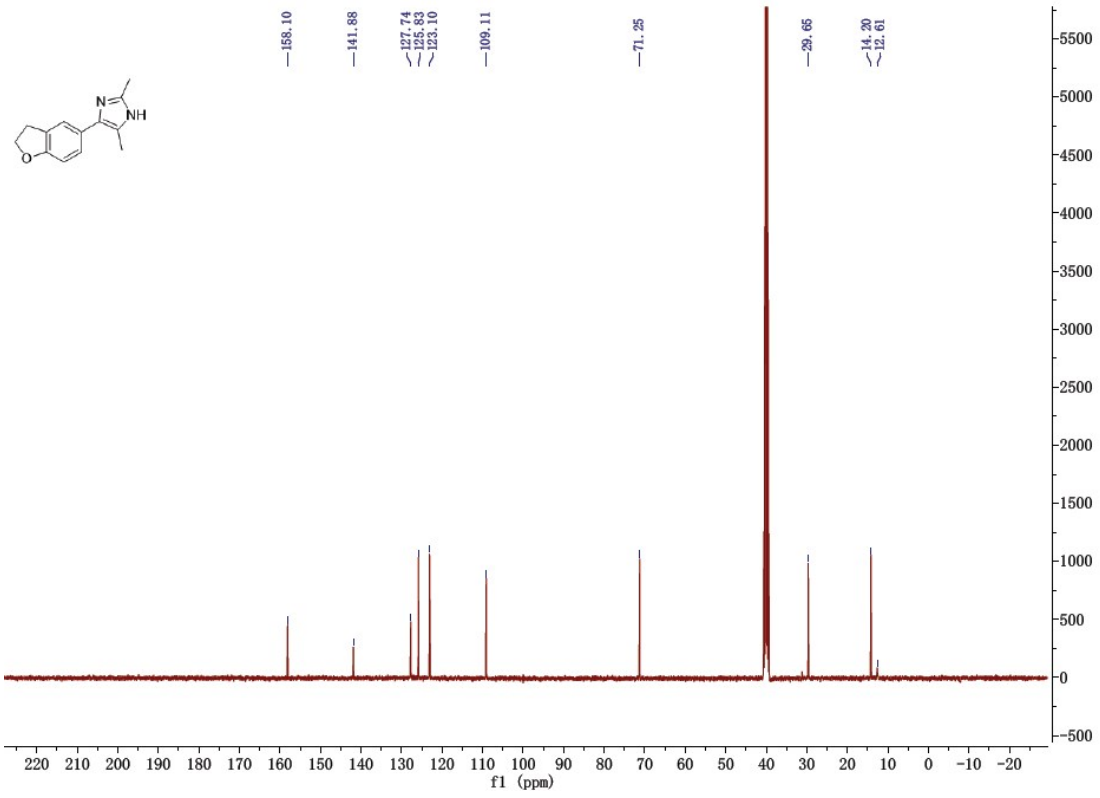
120.85
13.81
11.35
f1 (ppm)


7.39
7.25
7.23
6.76
6.74
4.53
4.51
4.49
3.20
3.18
3.16
2.24
2.22
1.08
1.16
1.00
2.43
2.59
3.12
3.09
f1 (ppm)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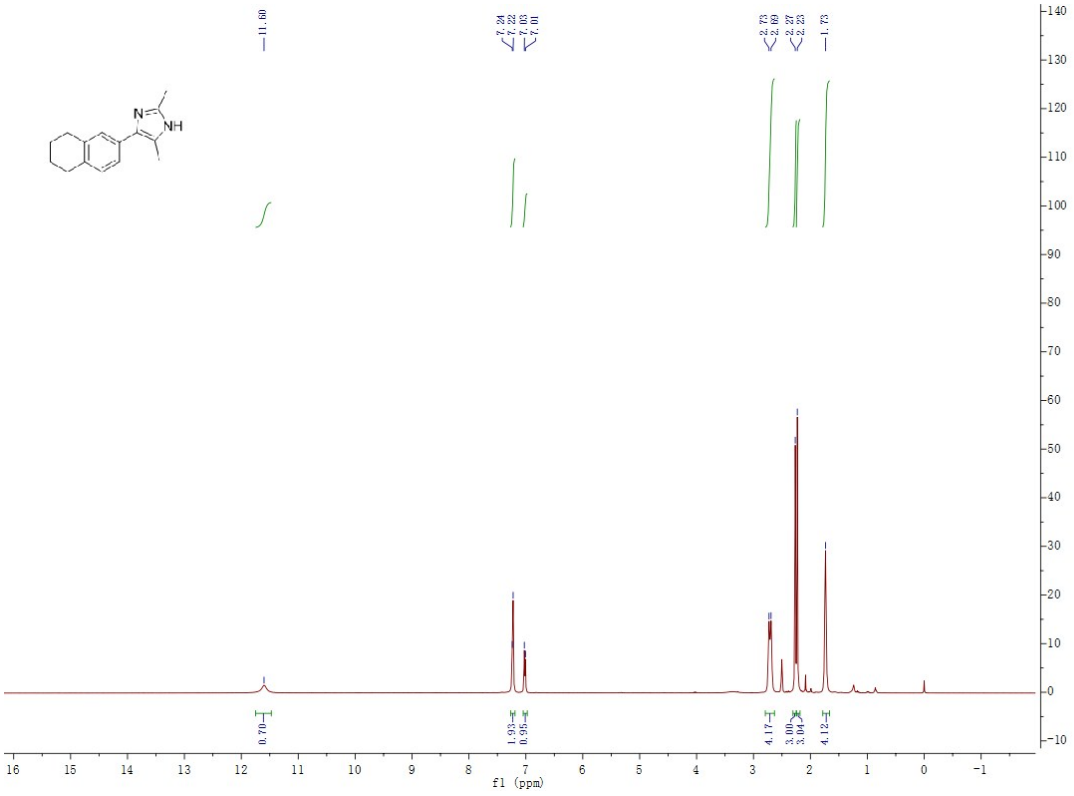
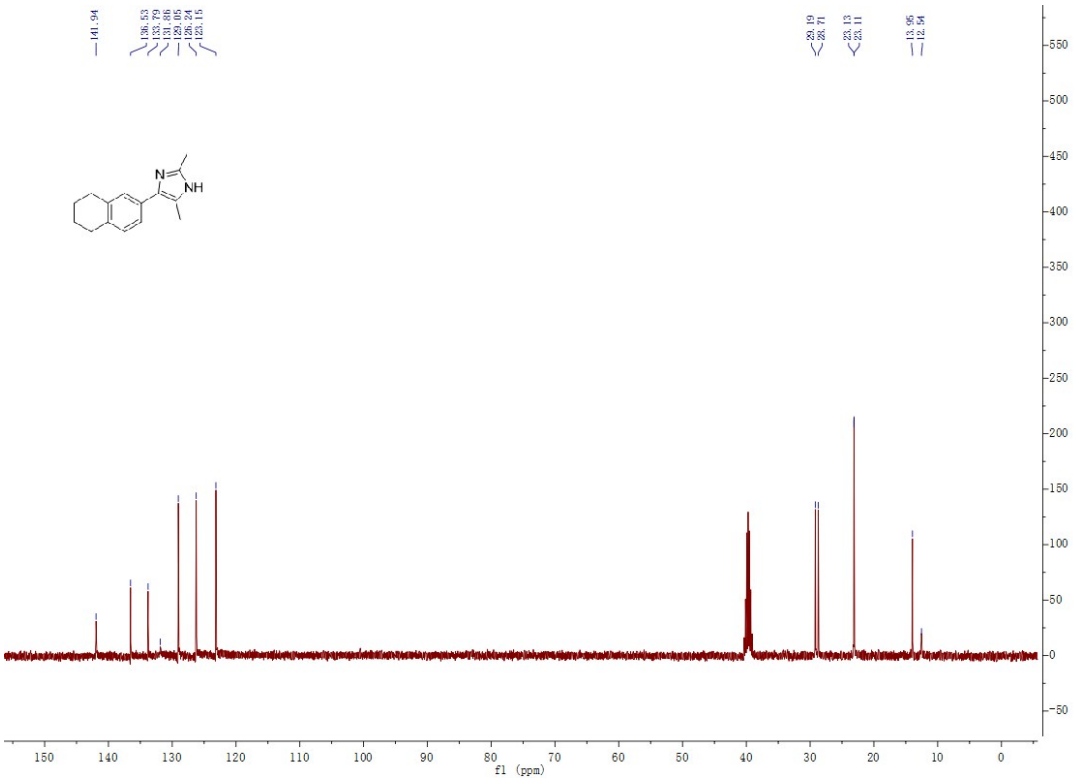
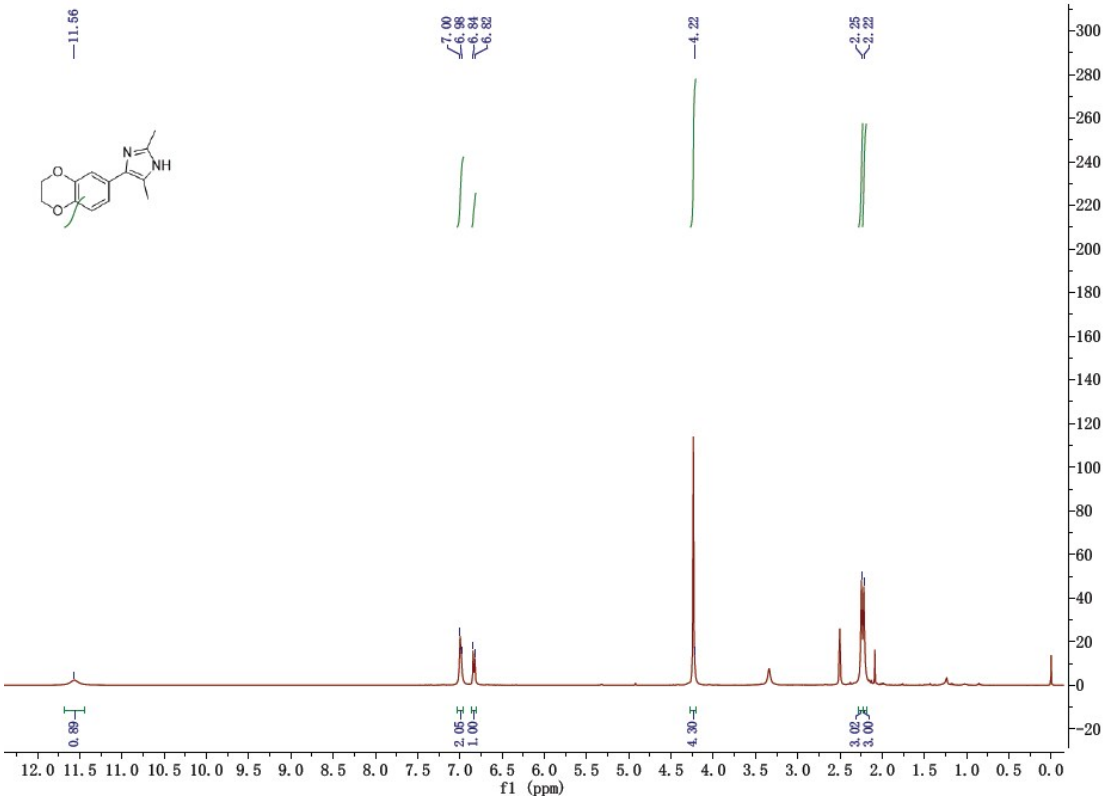
127.74
125.83
123.10
109.11
71.25
29.65
14.20
12.61
f1 (ppm)


11.60
7.24
7.22
7.03
7.01
2.73
2.69
2.27
2.23
1.73
0.70
1.93
0.95
4.17
3.00
3.04
4.12
f1 (ppm)


141.94
136.53
133.79
131.86
129.05
126.24
125.15
29.19
28.71
23.13
23.11
13.96
12.54
f1 (ppm)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6.98
6.84
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2.22
NH
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2.05
1.00
4.30
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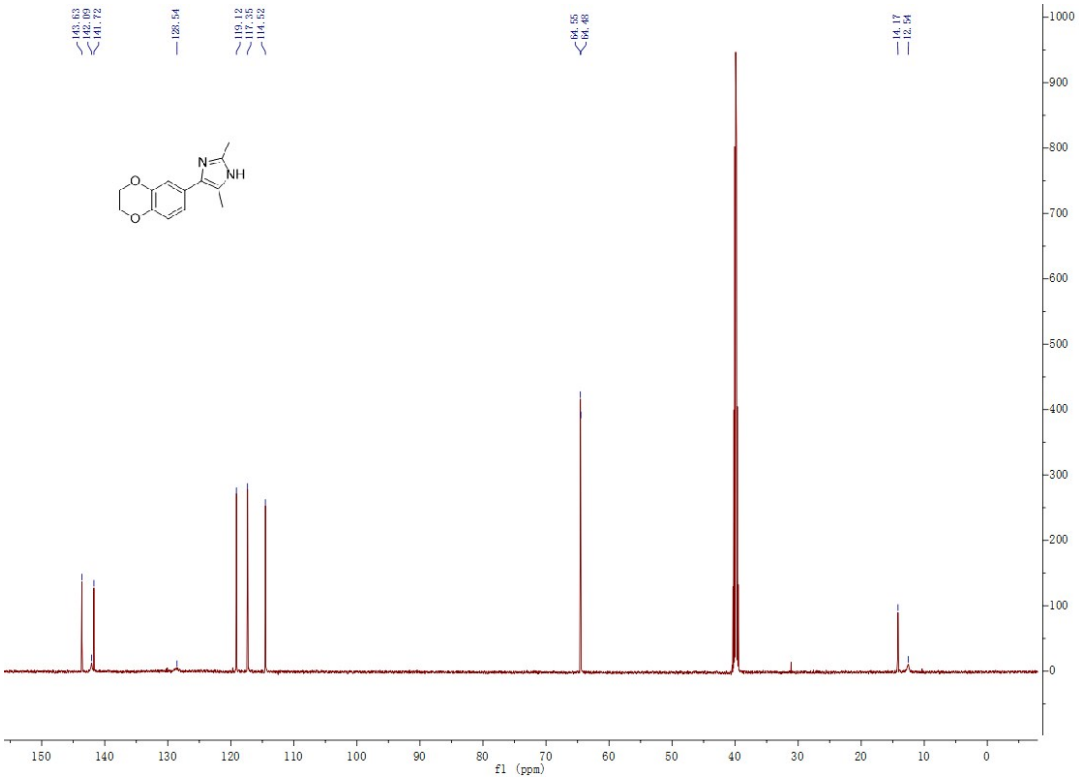
3.00
f1 (ppm)


145.63
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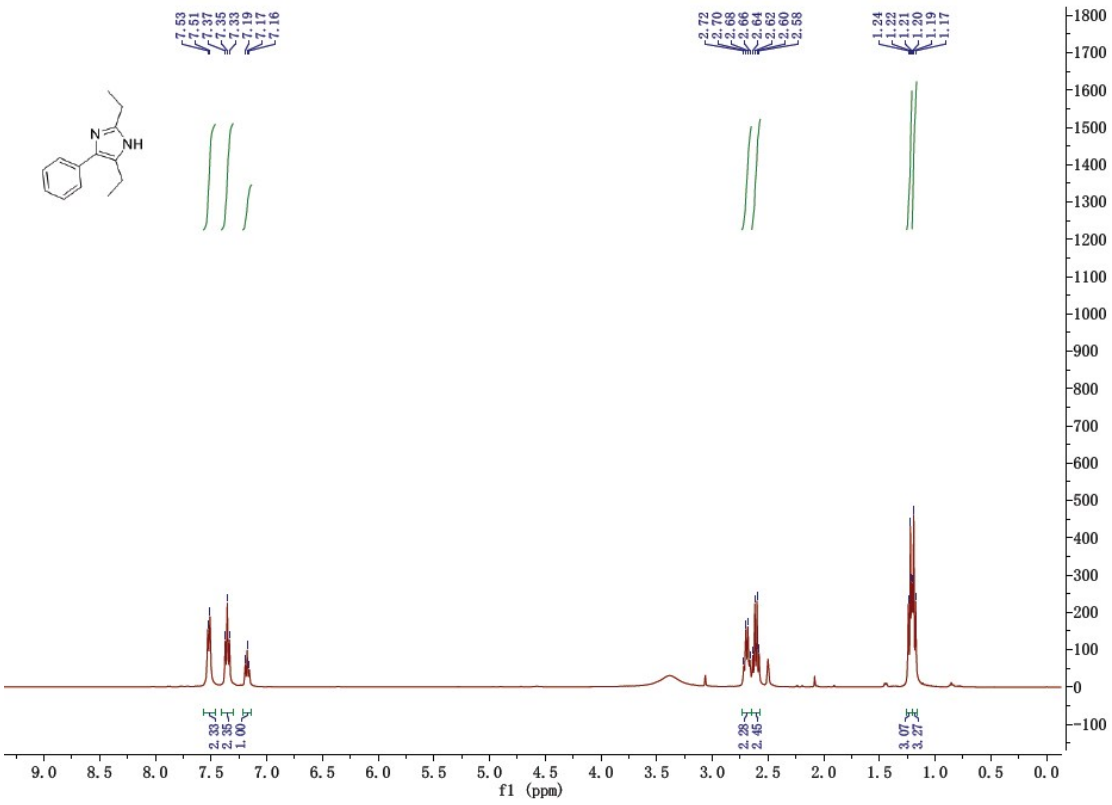
119.12
117.35
114.52
64.55
64.48
14.17
12.54
NH
f1 (ppm)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7.16
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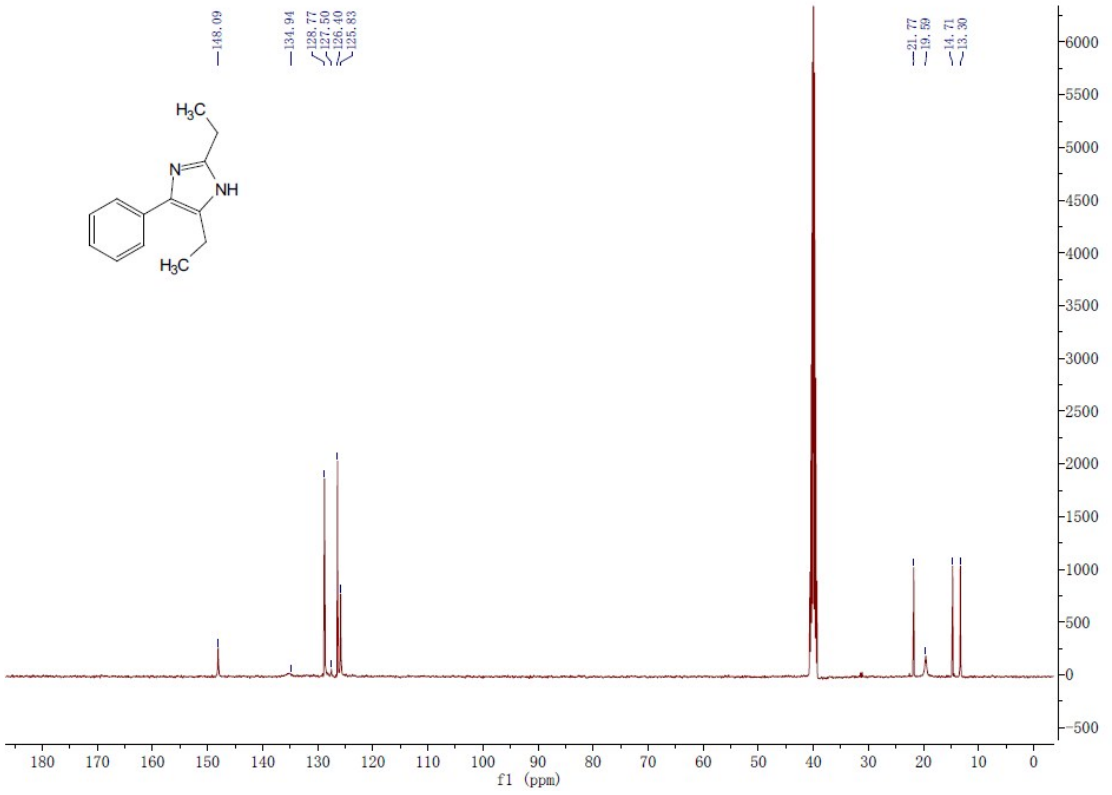
2.70
2.68
2.66
2.64
2.62
2.60
2.58
1.24
1.22
1.21
1.20
1.19
1.17
2.33
2.35
1.00
2.28
2.46
3.07
3.27
f1 (ppm)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125.83
21.77
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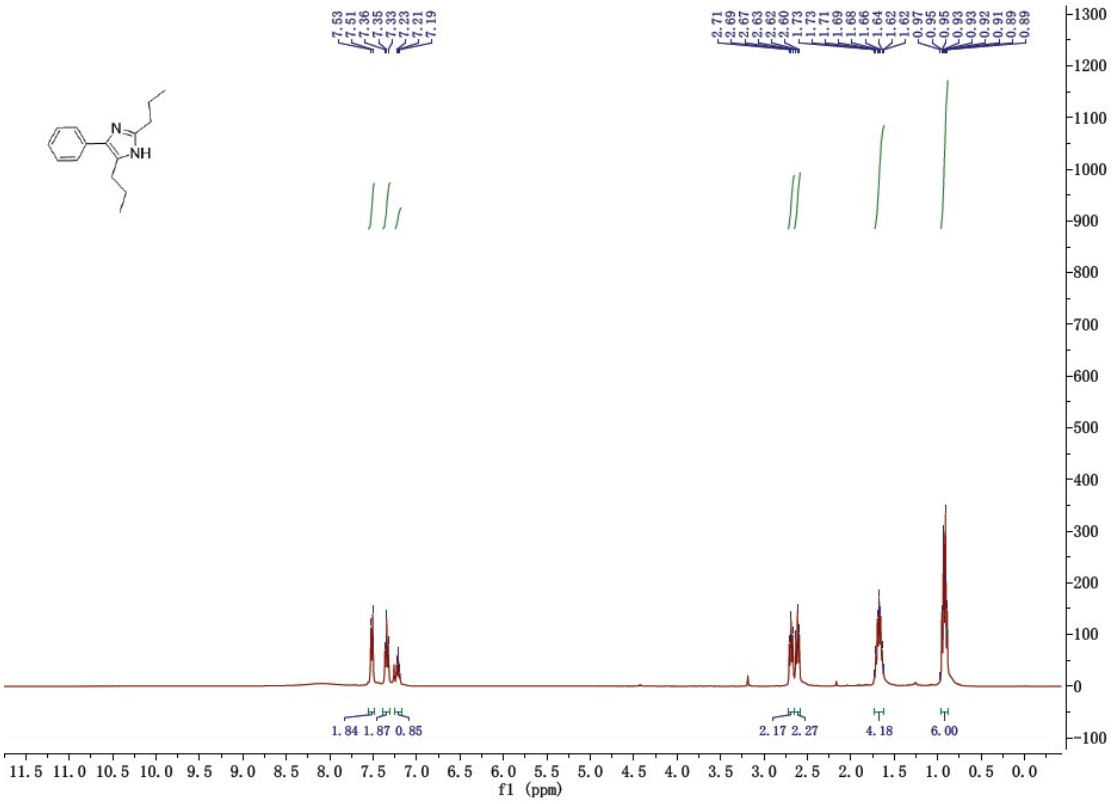
14.71
13.30
f1 (ppm)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7.51
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7.33
7.23
7.21
7.19
2.71
2.69
2.67
2.63
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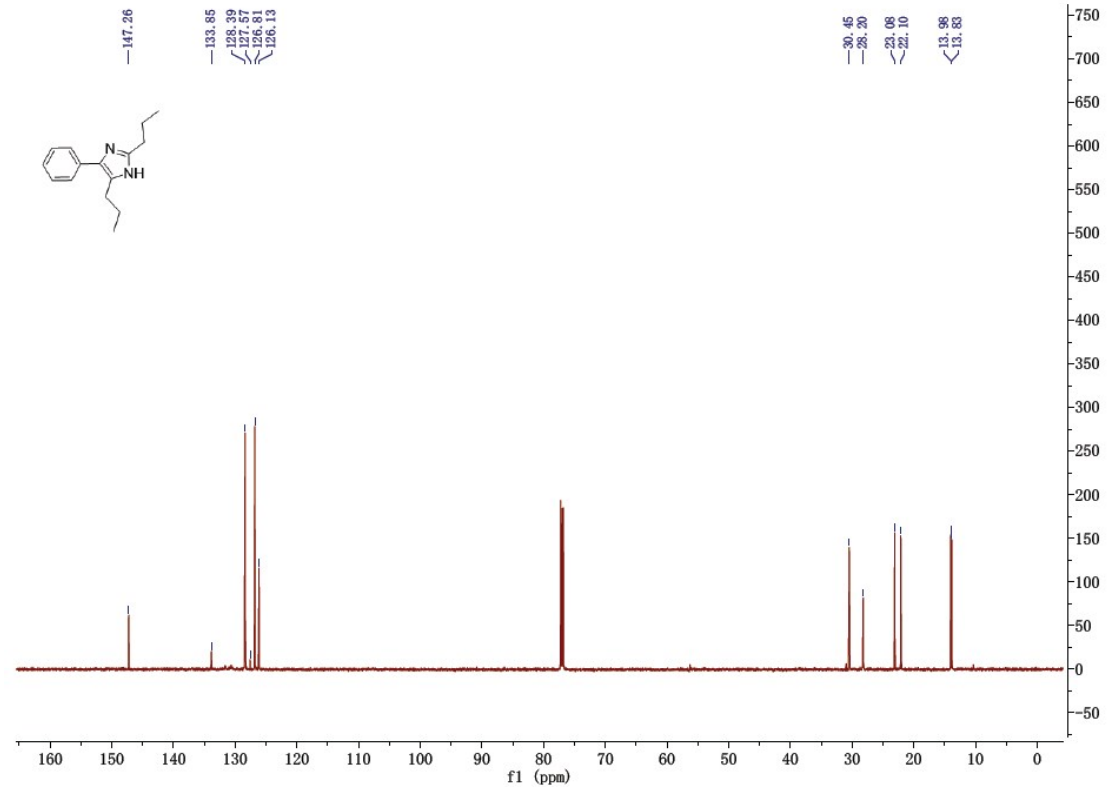
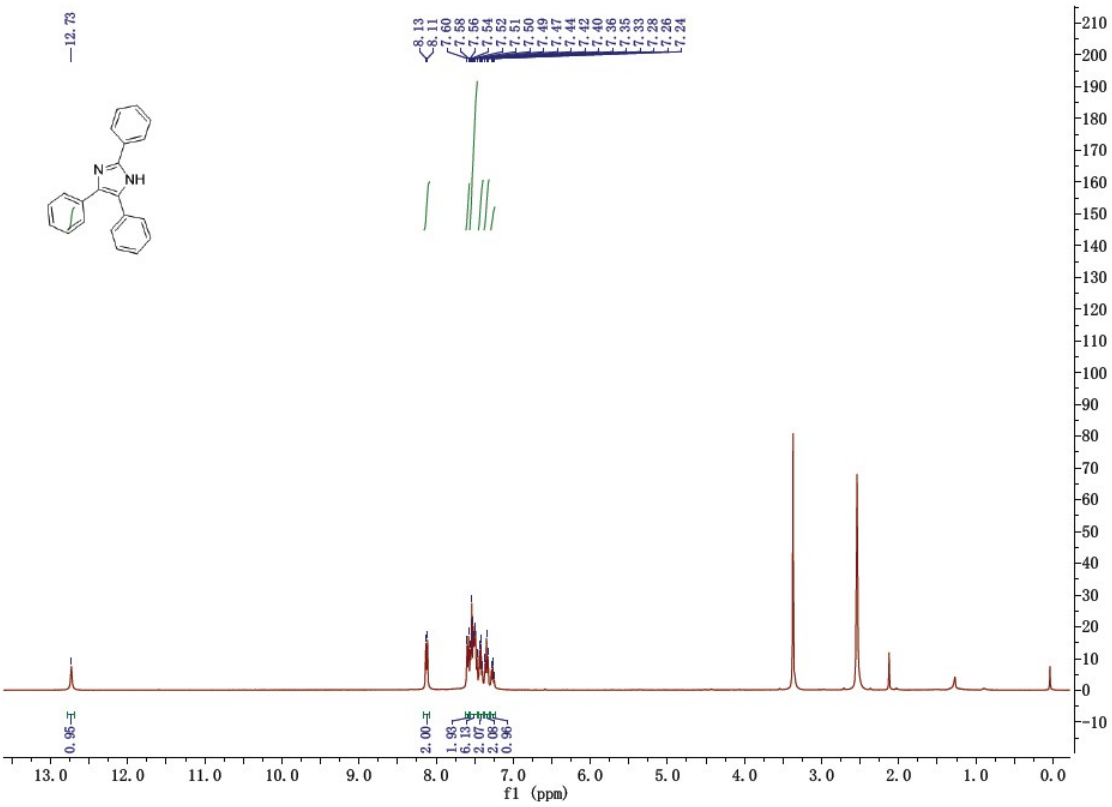
2.60
1.73
1.71
1.69
1.68
1.66
1.64
1.62
0.97
0.95
0.95
0.93
0.93
0.92
0.91
0.89
0.89
N
NH
1.84 1.87 0.85
2.17 2.27
4.18
6.00
f1 (ppm)


147.26
133.85
128.39
127.57
126.81
126.13
30.45
28.20
23.06
22.10
13.98
13.83
N
NH
f1 (ppm)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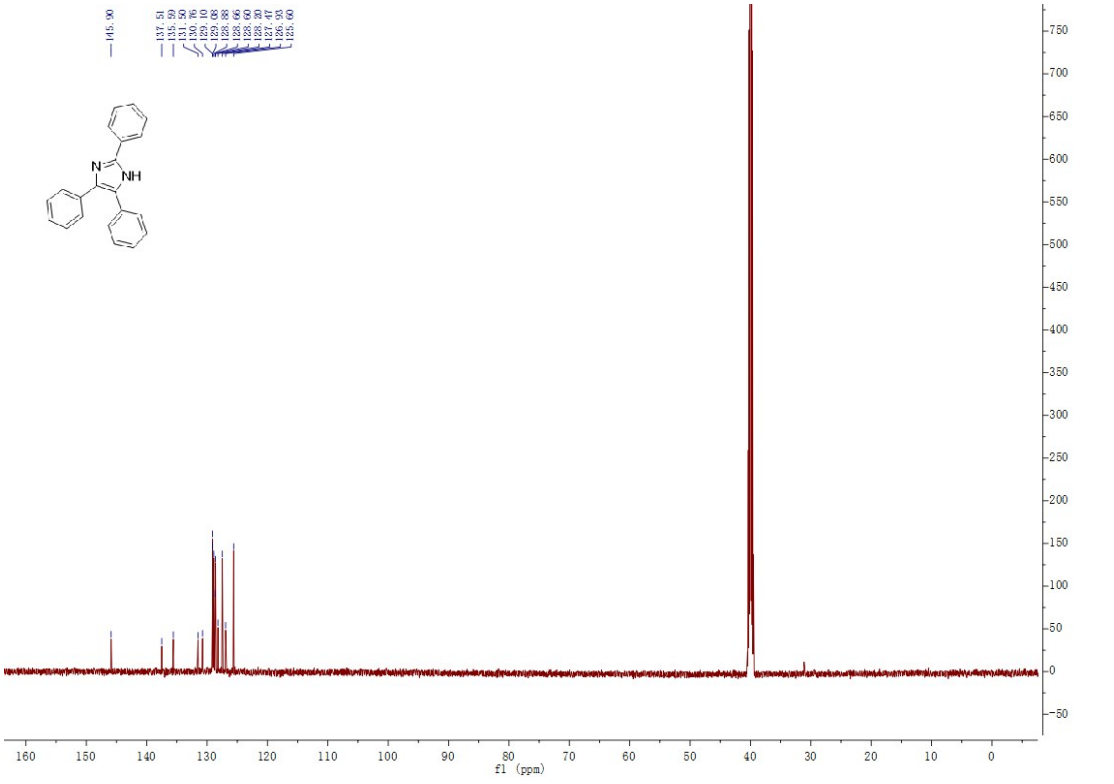
7.56
7.54
7.52
7.51
7.50
7.49
7.47
7.44
7.42
7.40
7.36
7.35
7.33
7.28
7.26
7.24
NH
0.95
2.00
1.93
6.13
2.07
2.08
0.90
f1 (ppm)


145.90
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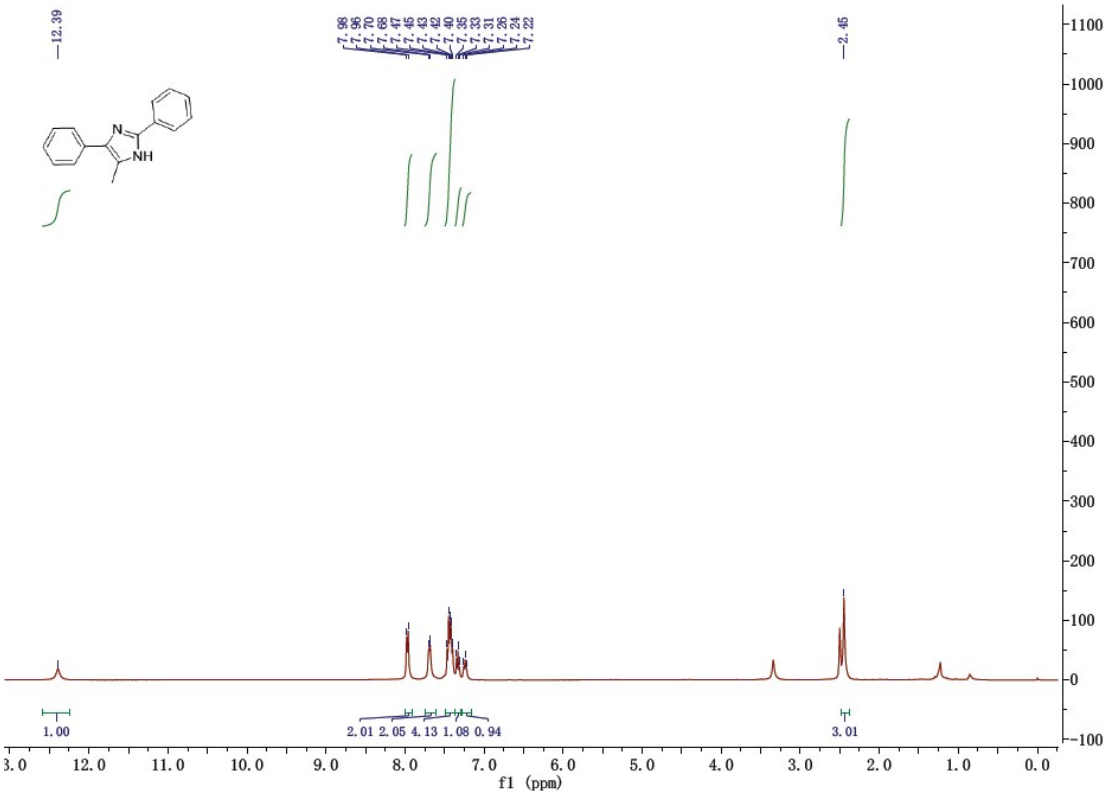
135.99
131.54
130.76
129.10
129.08
128.98
128.66
128.60
128.20
127.47
126.93
125.60
NH
f1 (ppm)


12.39
7.98
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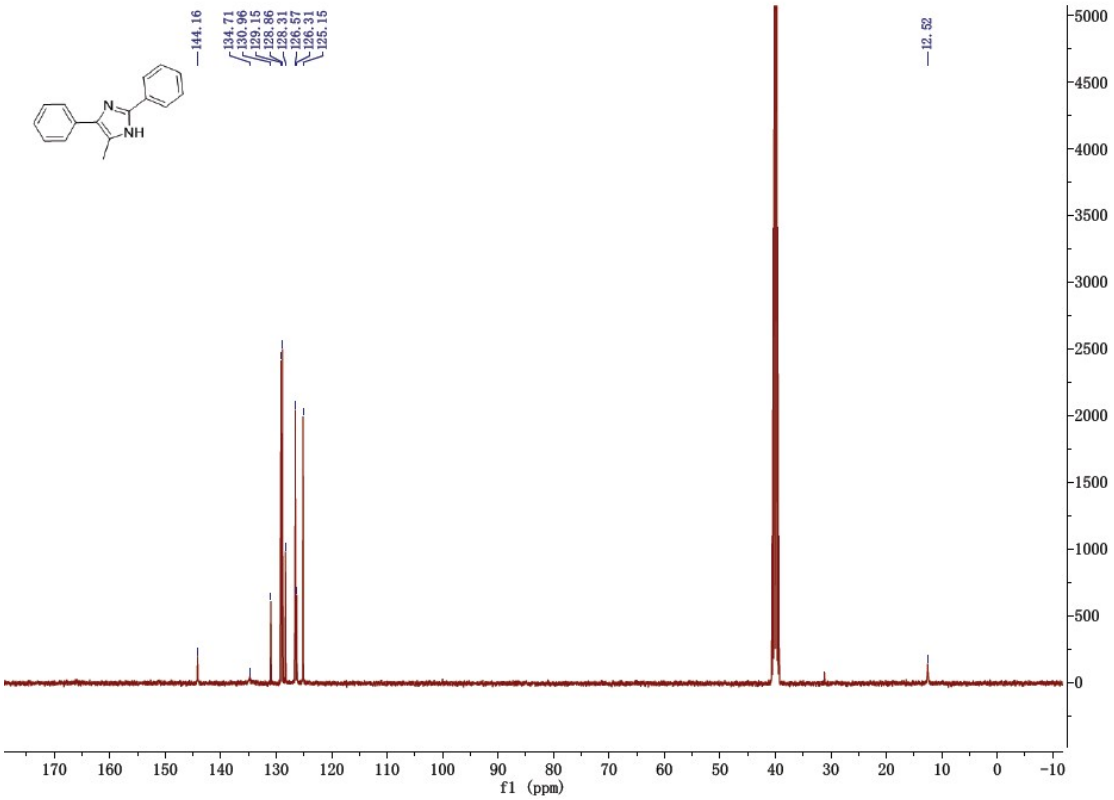
7.47
7.45
7.43
7.42
7.40
7.35
7.33
7.31
7.26
7.24
7.22
2.45
N
NH
1.00
2.01 2.05 4.13 1.08 0.94
3.01
f1 (ppm)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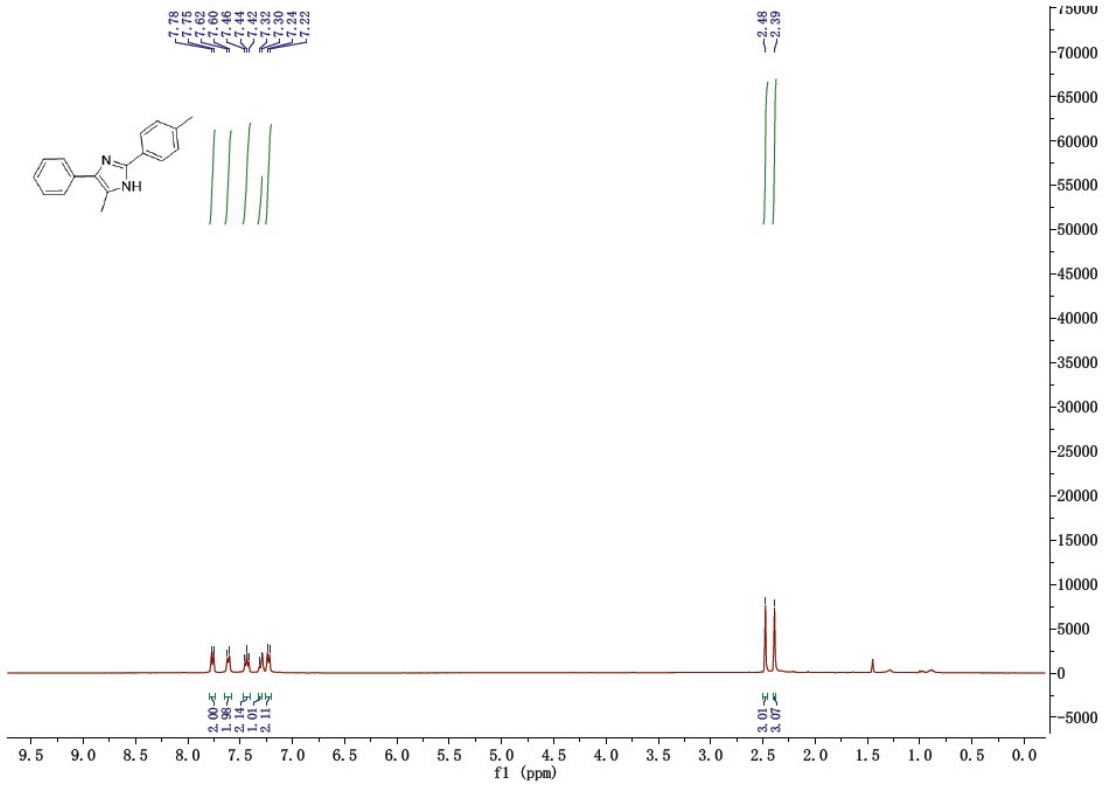
128.31
126.57
126.31
125.15
12.52
N
NH
f1 (ppm)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7.44
7.42
7.32
7.30
7.24
7.22
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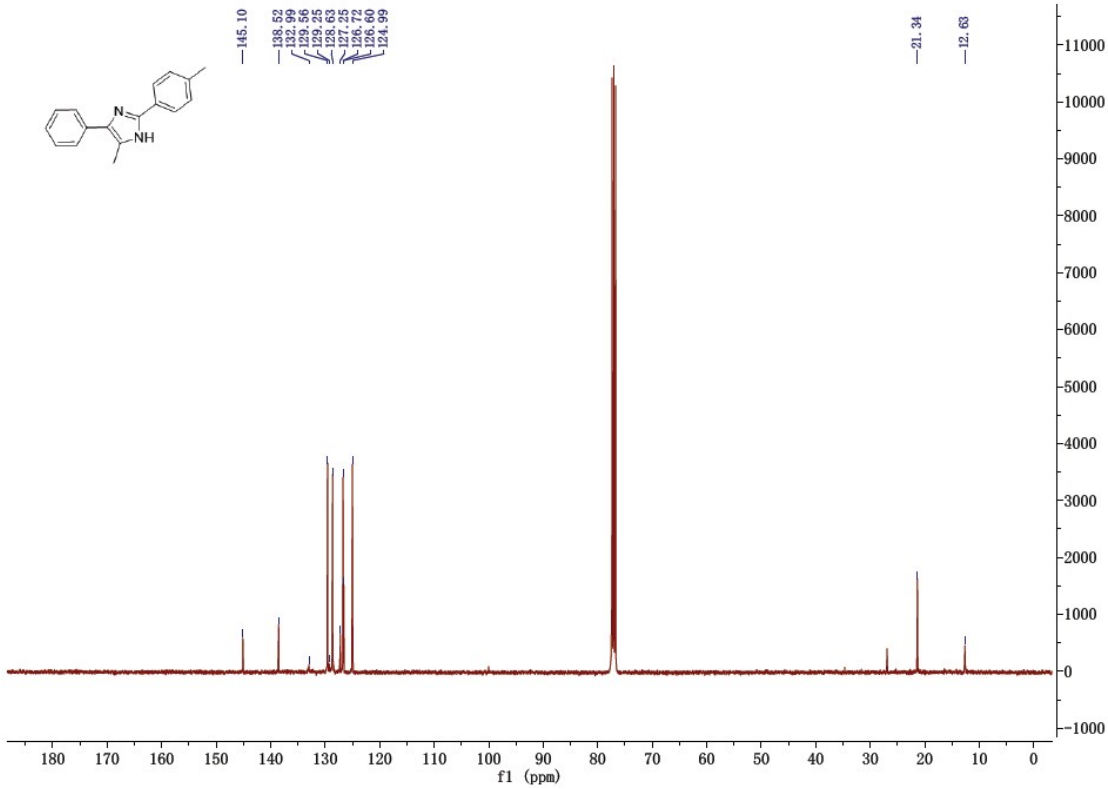
2.39
N
NH
2.00
1.98
2.14
1.01
2.11
3.01
3.07
f1 (ppm)


145.10
138.52
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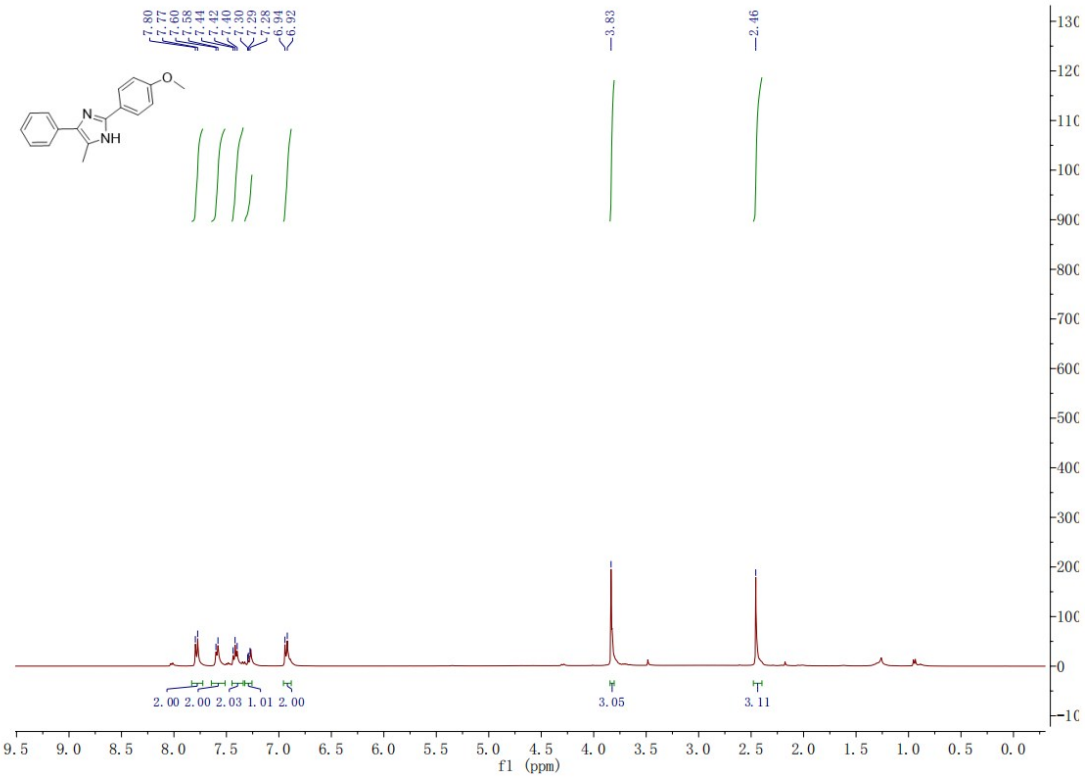
129.56
129.25
128.63
127.25
126.72
126.60
124.99
21.34
12.63
N
NH
f1 (ppm)


7.80
7.77
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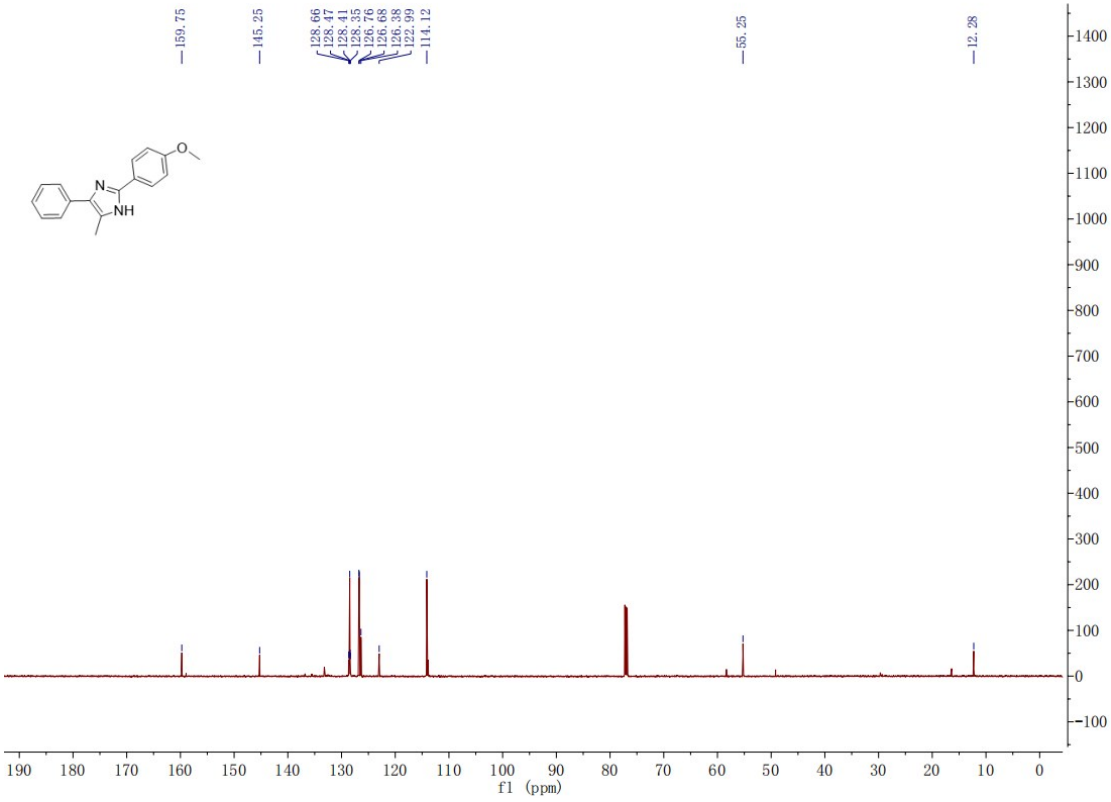
7.44
7.42
7.40
7.30
7.29
7.28
6.94
6.92
3.83
2.46
O
N
NH
2.00 2.00 2.03 1.01 2.00
3.05
3.11
f1 (ppm)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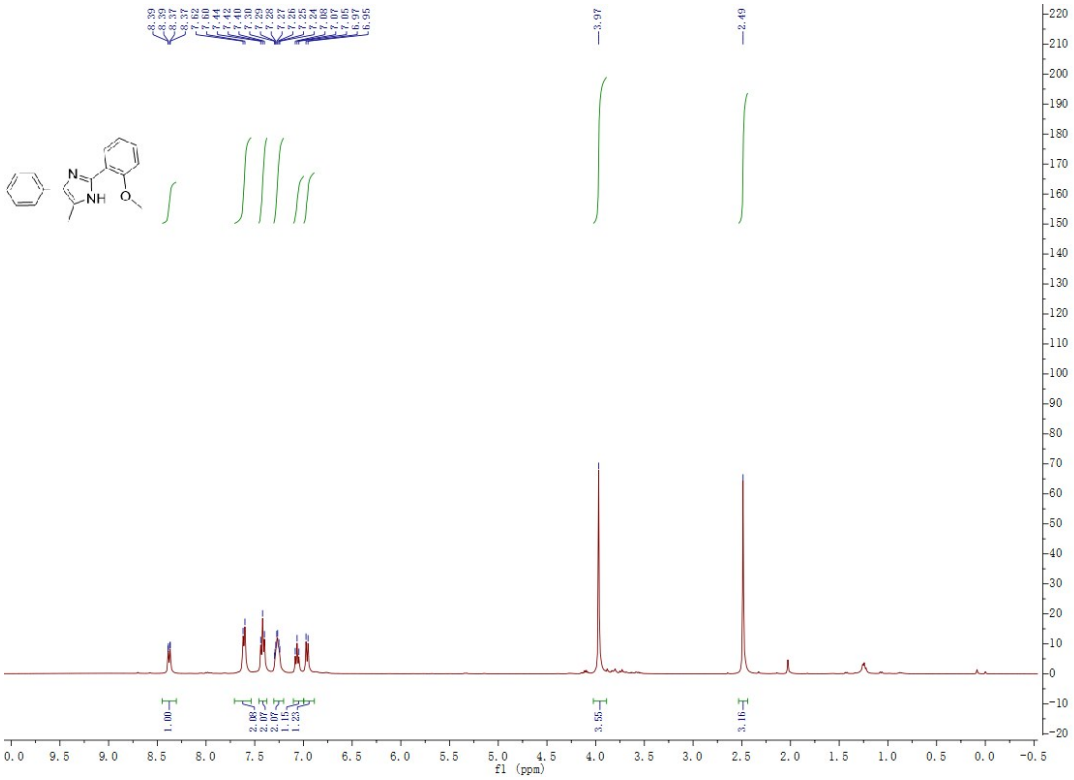
128.35
126.76
126.68
126.38
122.99
114.12
55.25
12.28
O
N
NH
f1 (ppm)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7.29
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7.27
7.26
7.25
7.24
7.09
7.07
7.05
6.97
6.95
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NH
O
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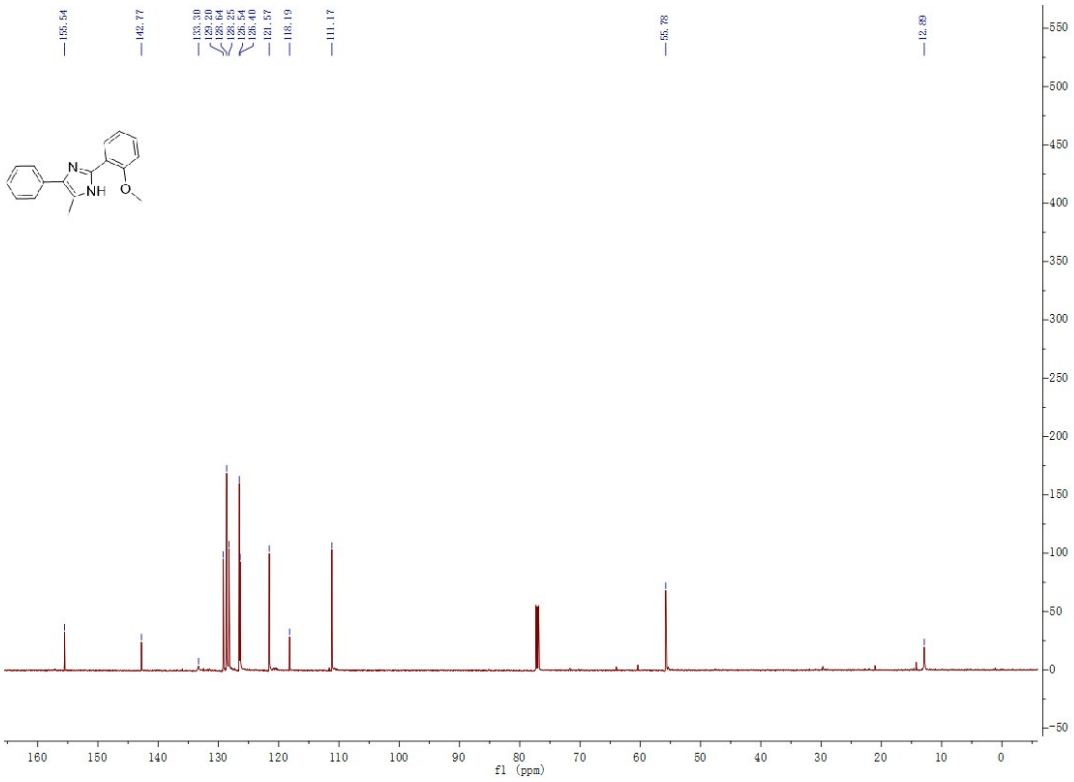
2.08
2.07
1.15
1.27
3.55
3.16
f1 (ppm)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111.17
55.78
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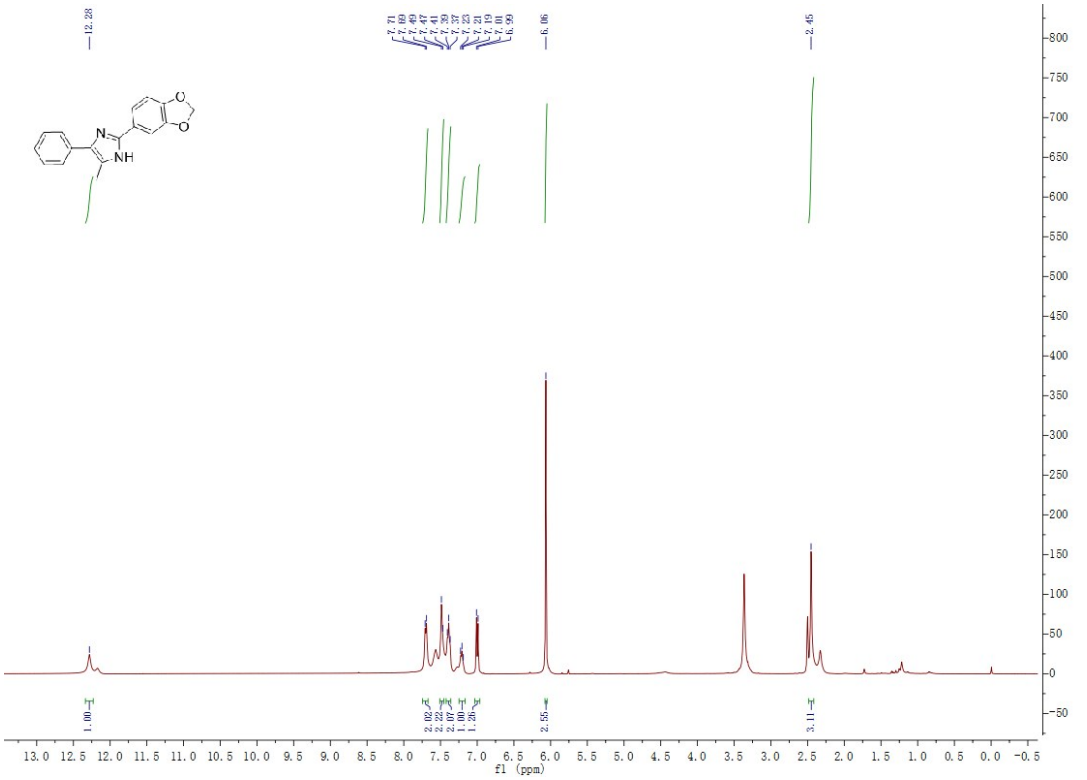
NH
O
f1 (ppm)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7.44
7.39
7.37
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7.21
7.19
7.01
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6.06
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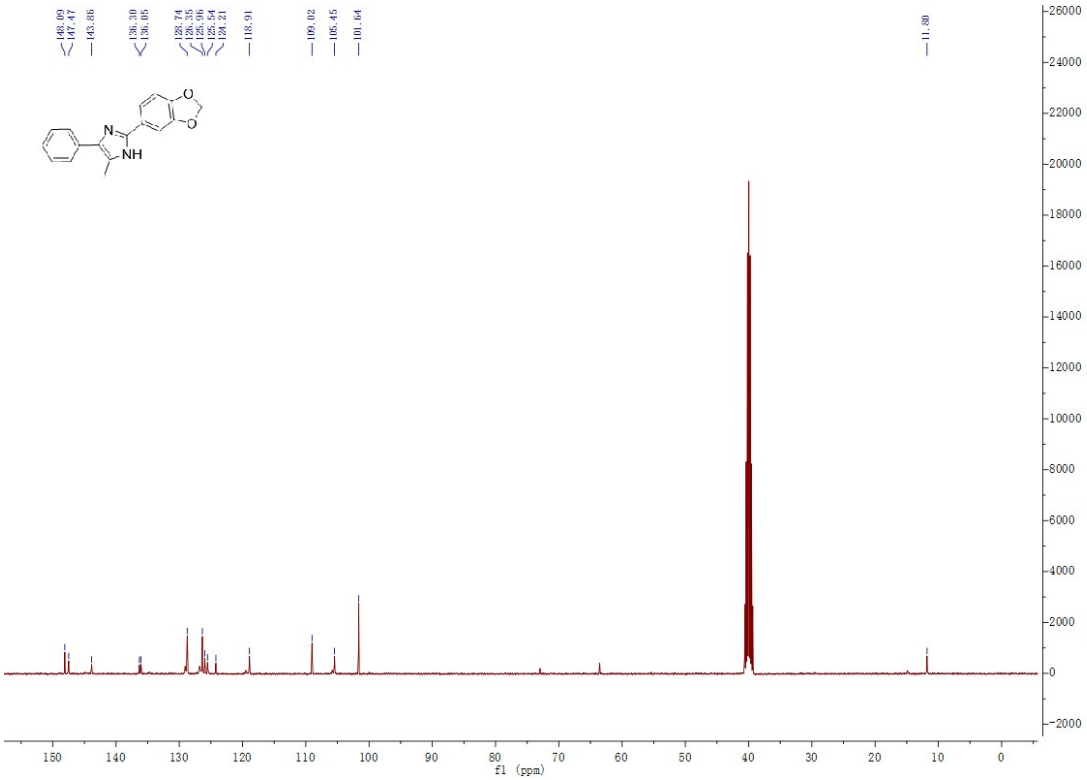
1.00
2.02
2.22
2.05
1.00
1.26
2.55
3.11
f1 (ppm)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124.21
118.91
109.02
105.45
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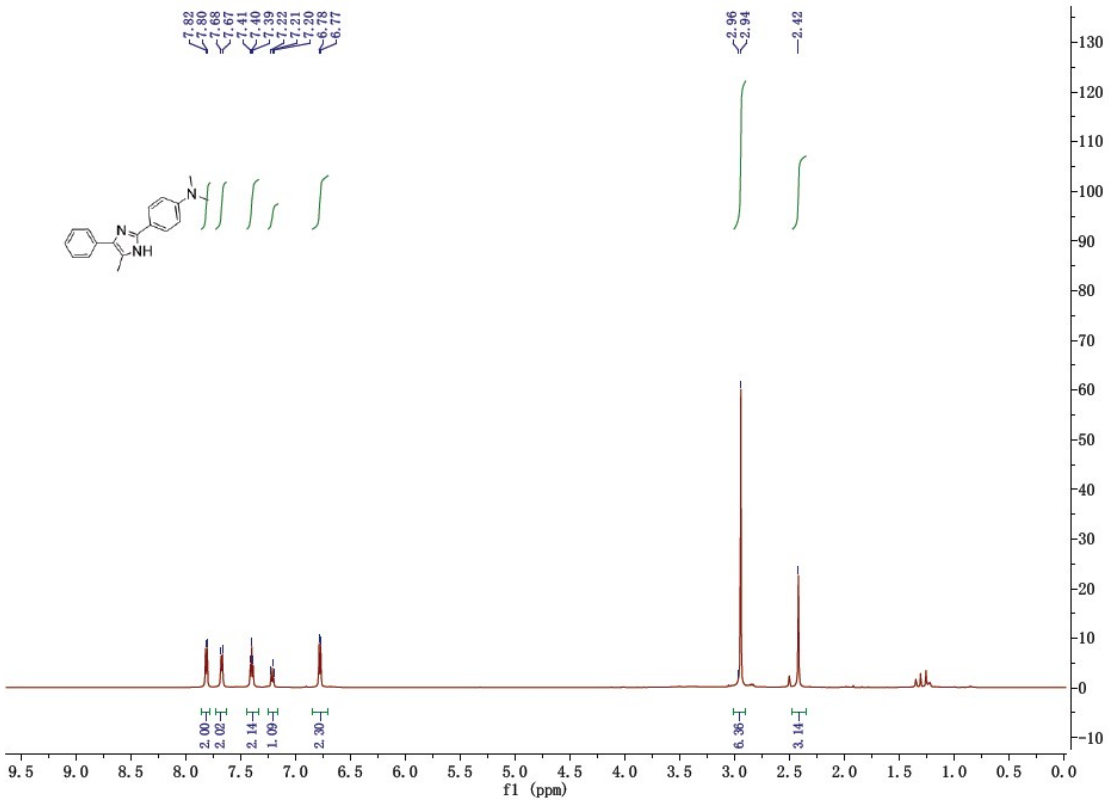
11.80
f1 (ppm)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7.40
7.39
7.22
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7.20
6.78
6.77
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2.02
2.14
1.09
2.30
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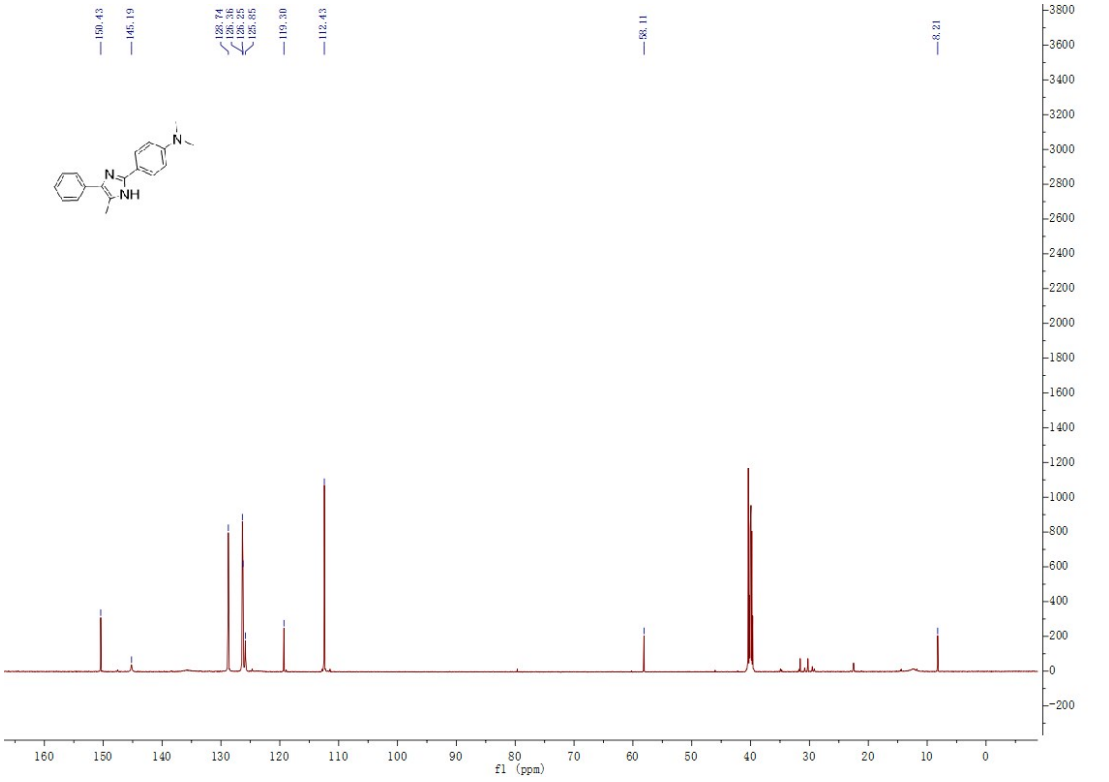
3.14
f1 (ppm)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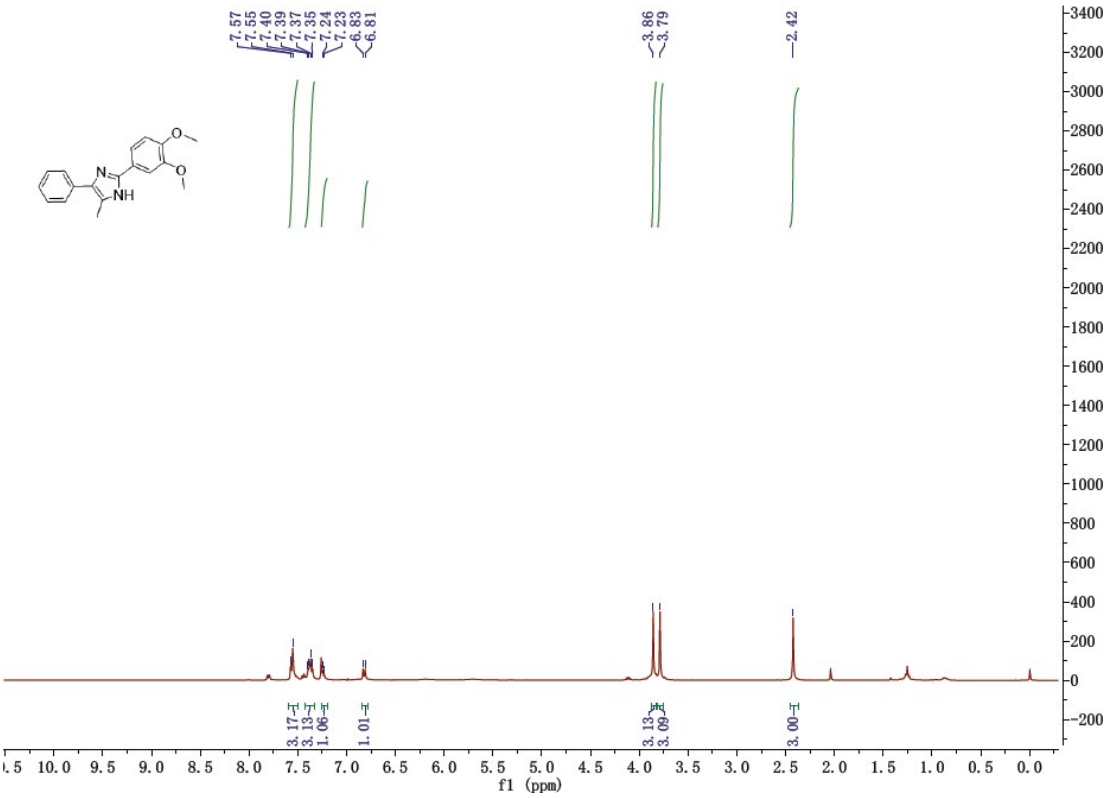
68.11
8.21
f1 (ppm)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7.23
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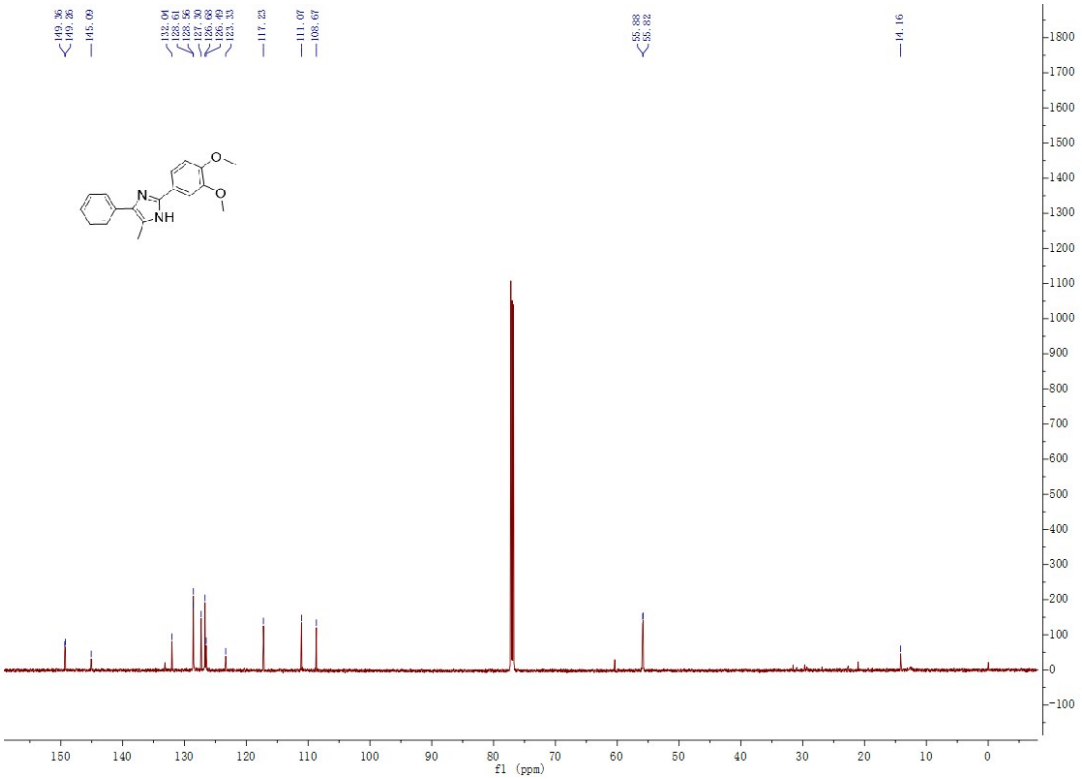
3.13
1.06
1.01
3.13
3.09
3.00
f1 (ppm)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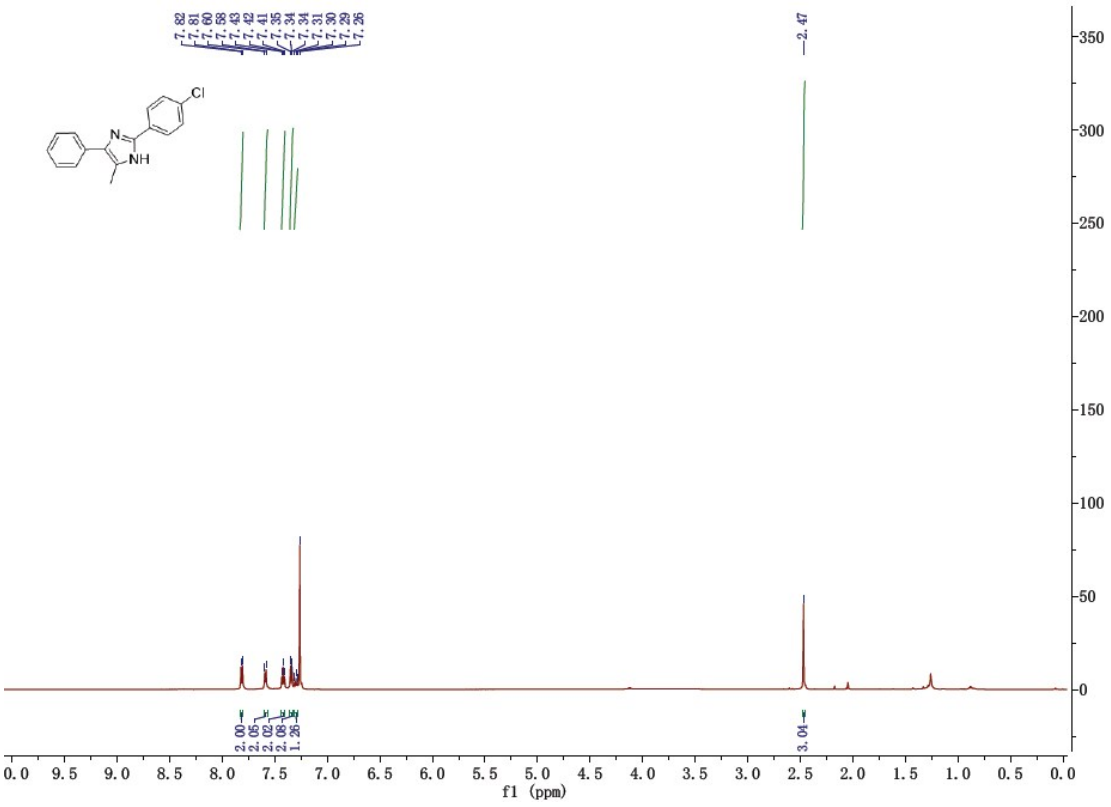
111.07
108.67
55.88
55.82
14.16
f1 (ppm)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7.42
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7.35
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7.34
7.31
7.30
7.29
7.26
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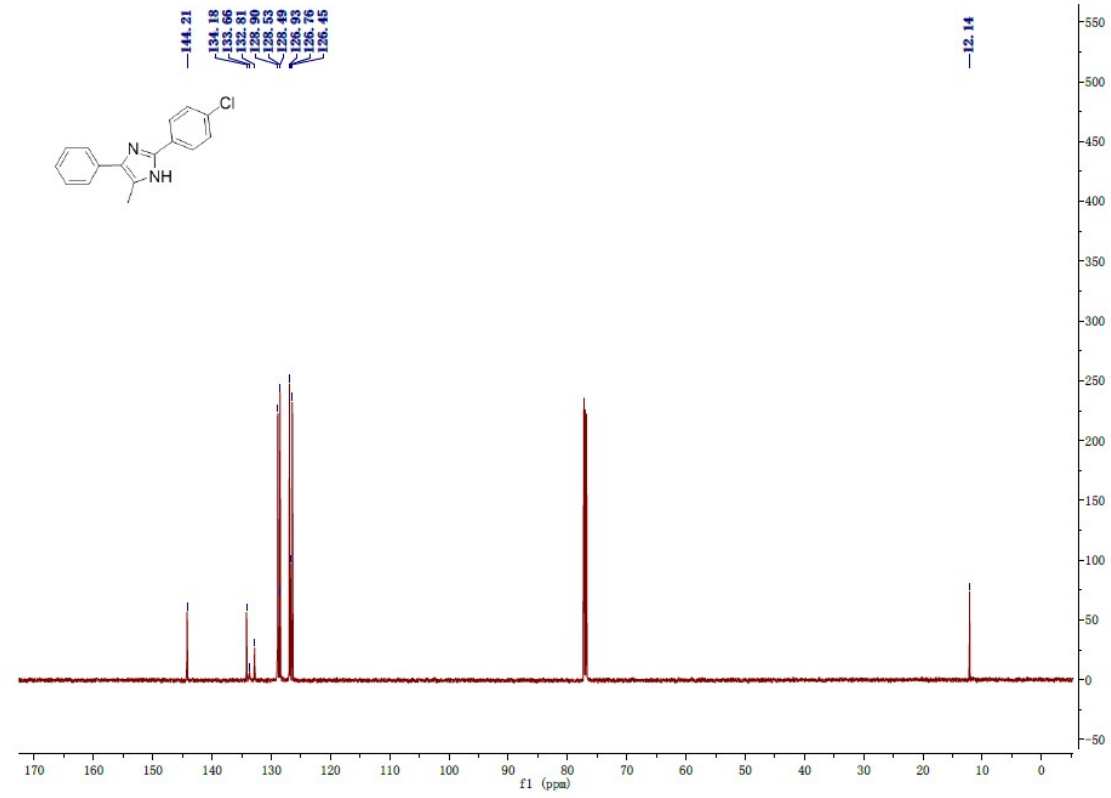
2.05
2.02
2.08
1.28
3.04
f1 (ppm)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134.18
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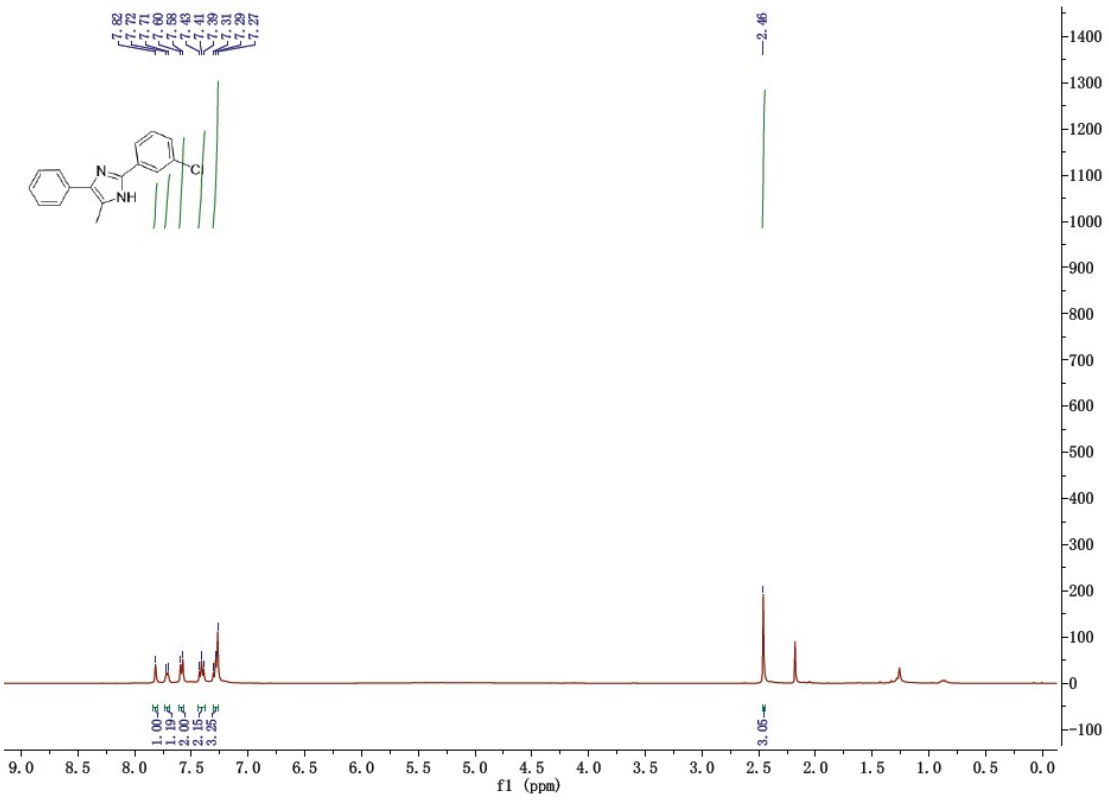
129.53
128.49
128.33
126.76
126.45
12.14
Cl
N
NH
f1 (ppm)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7.43
7.41
7.39
7.31
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7.27
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NH
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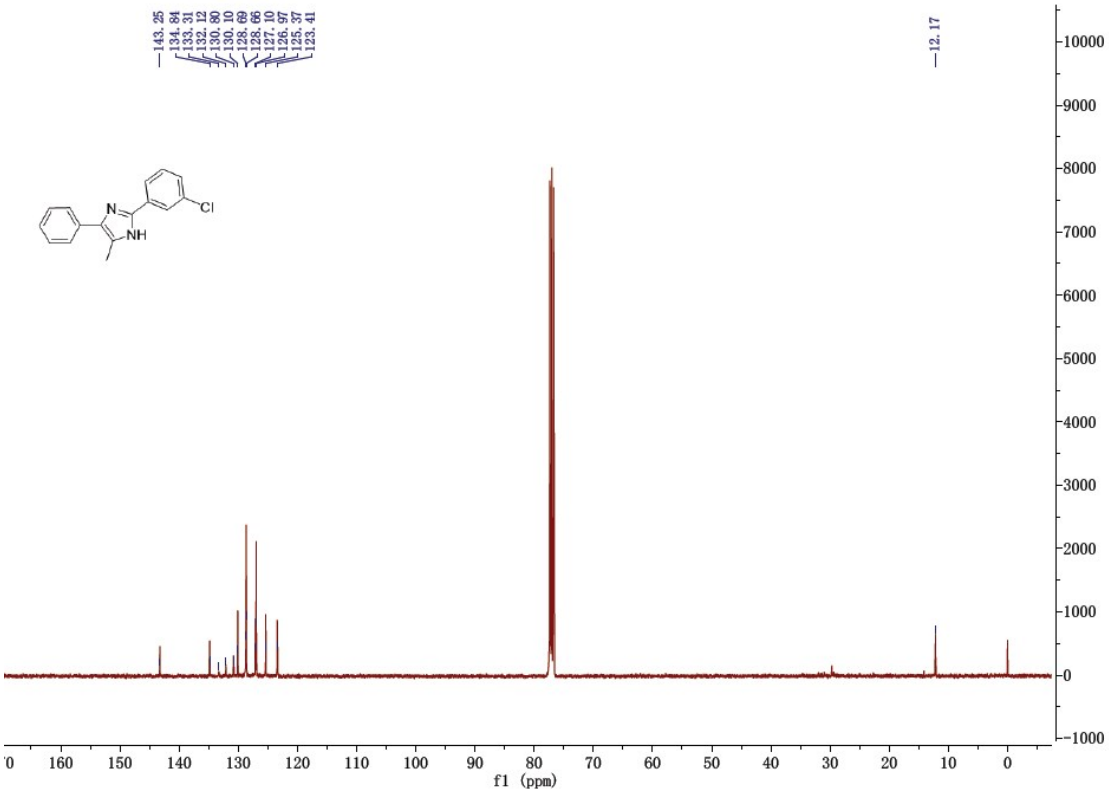
1.00
2.15
3.25
3.05
f1 (ppm)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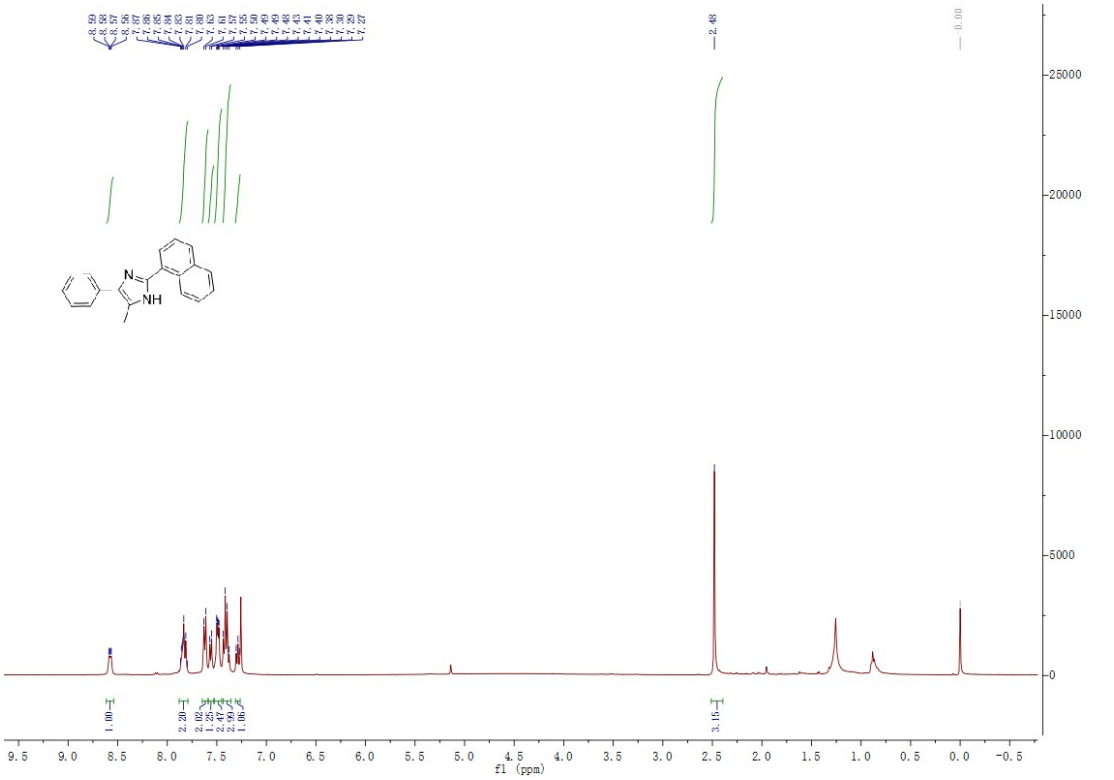
125.57
123.41
12.17
N
NH
Cl
f1 (ppm)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7.80
7.65
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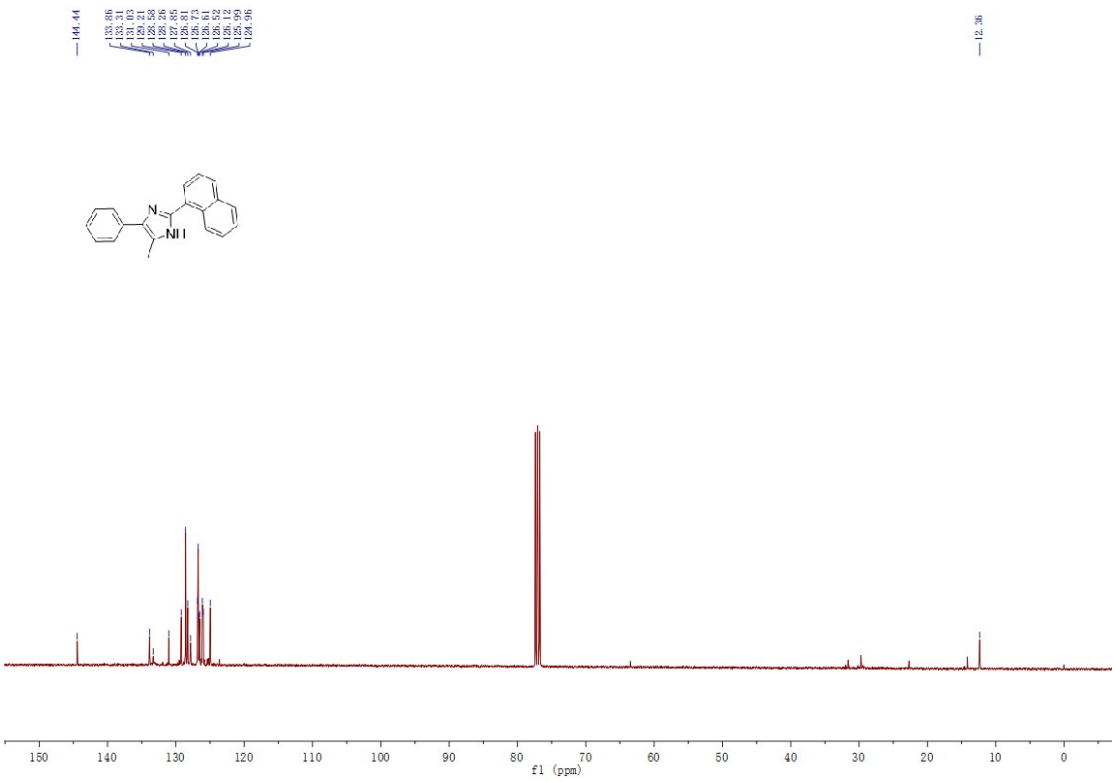
7.50
7.49
7.48
7.45
7.43
7.40
7.38
7.30
7.29
7.27
2.48
0.00
N
NH
25000
20000
15000
10000
5000
0
1.00
2.20
2.05
2.47
2.99
1.06
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.58
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126.81
126.73
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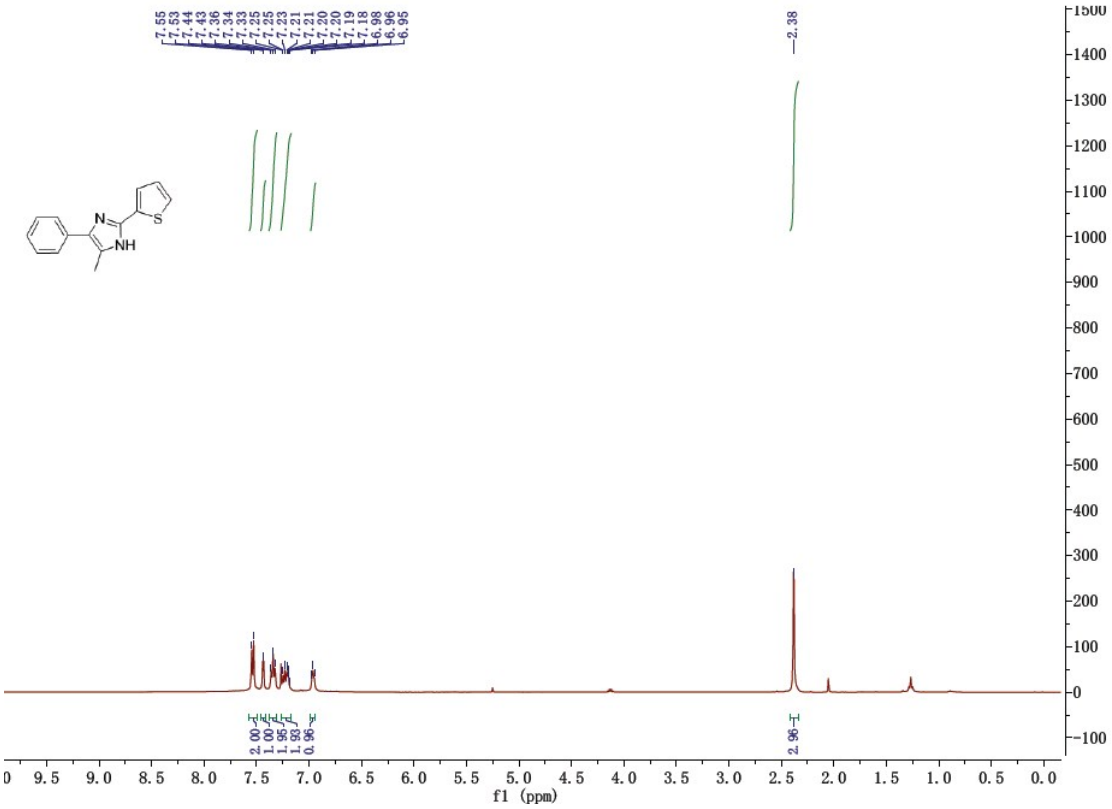
125.95
124.96
12.36
N
NH
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.23
7.21
7.21
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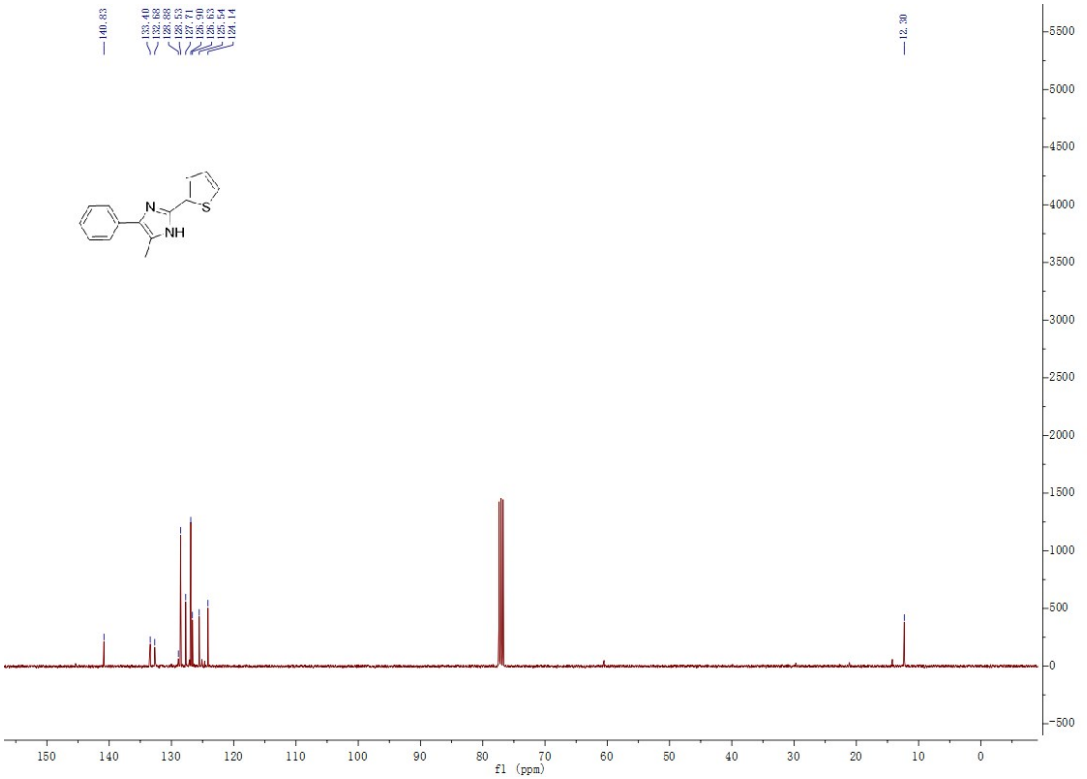
7.19
7.18
6.98
6.96
6.95
2.38
N
S
NH
2.00
1.00
1.95
1.88
0.96
2.96
f1 (ppm)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127.71
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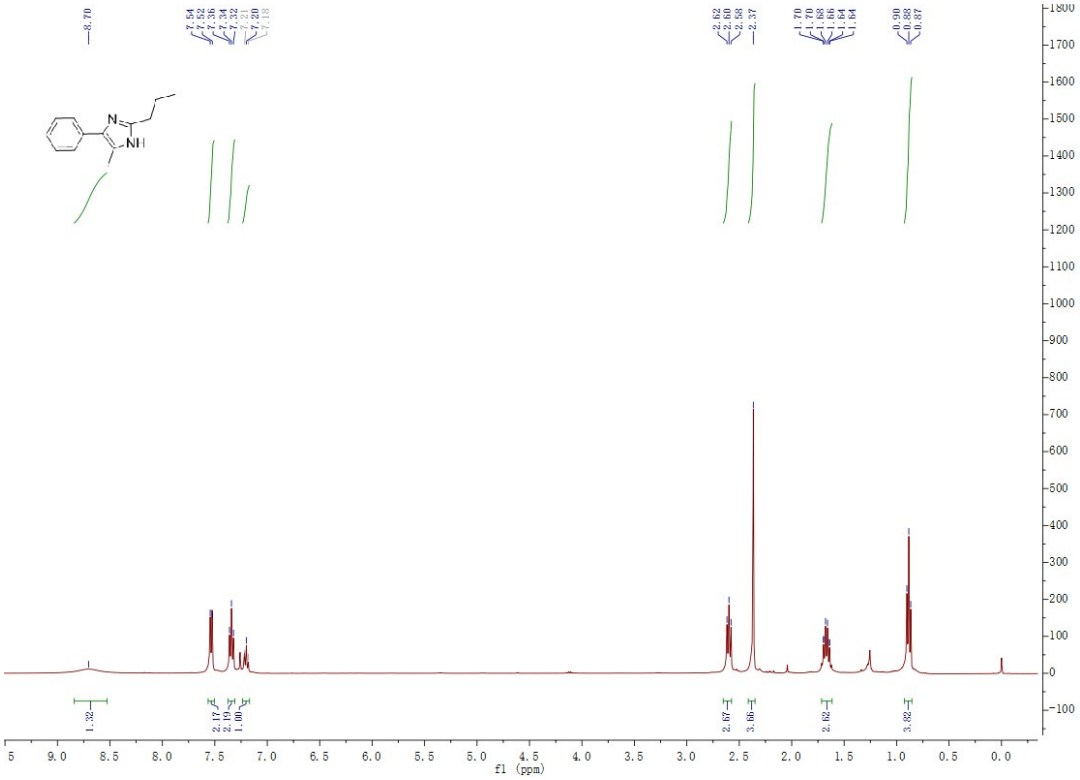
126.65
125.54
124.14
12.30
N
S
NH
f1 (ppm)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7.20
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2.60
2.58
2.37
1.70
1.68
1.66
1.64
1.64
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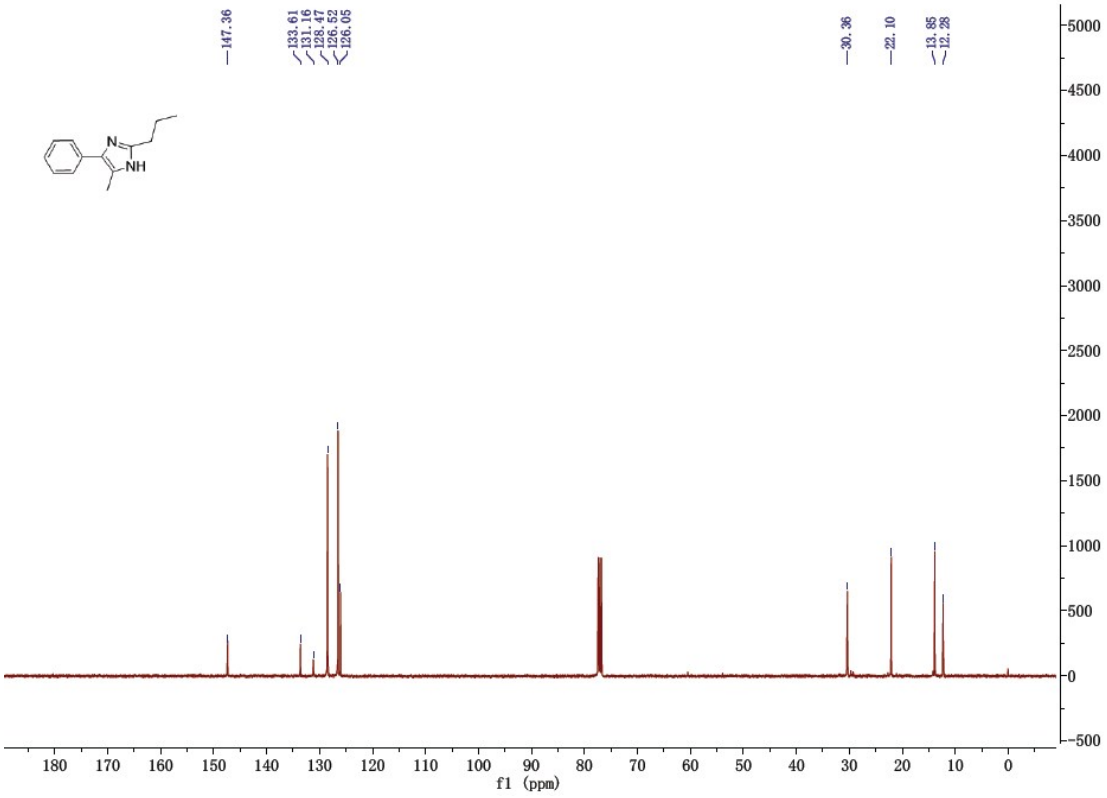
0.87
1.32
2.17
2.19
1.00
2.67
3.06
2.62
3.82
f1 (ppm)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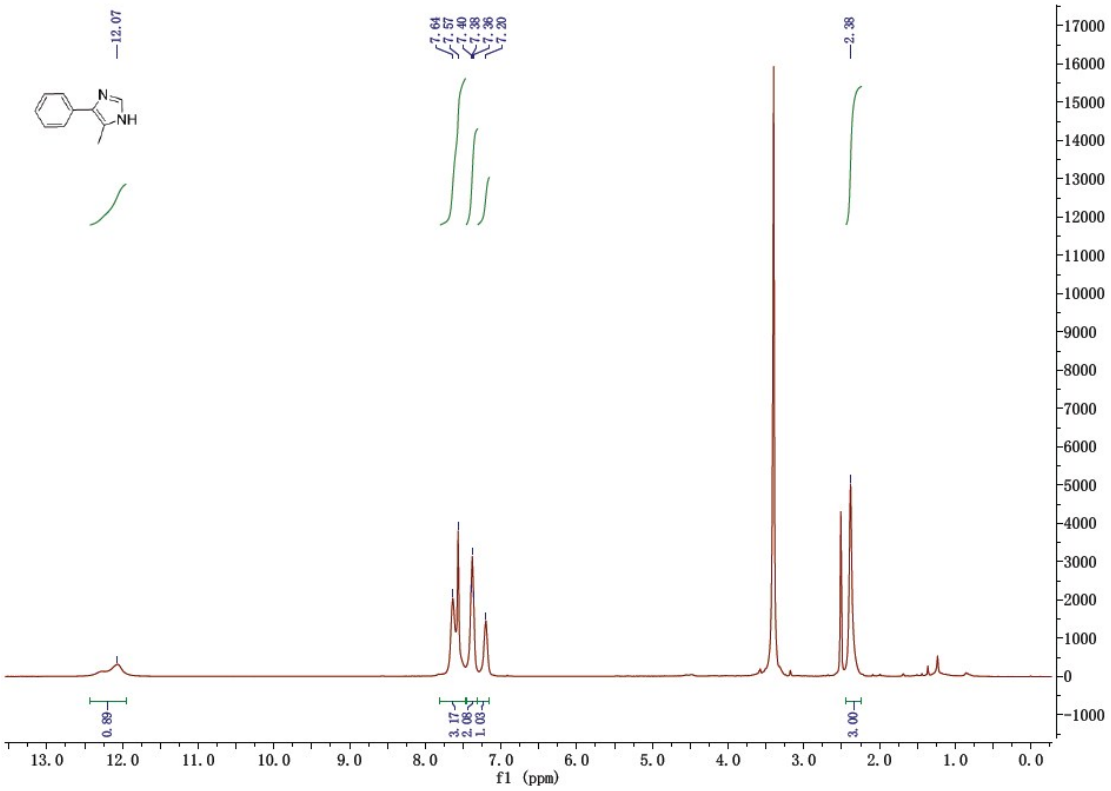
12.28
f1 (ppm)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7.20
2.38
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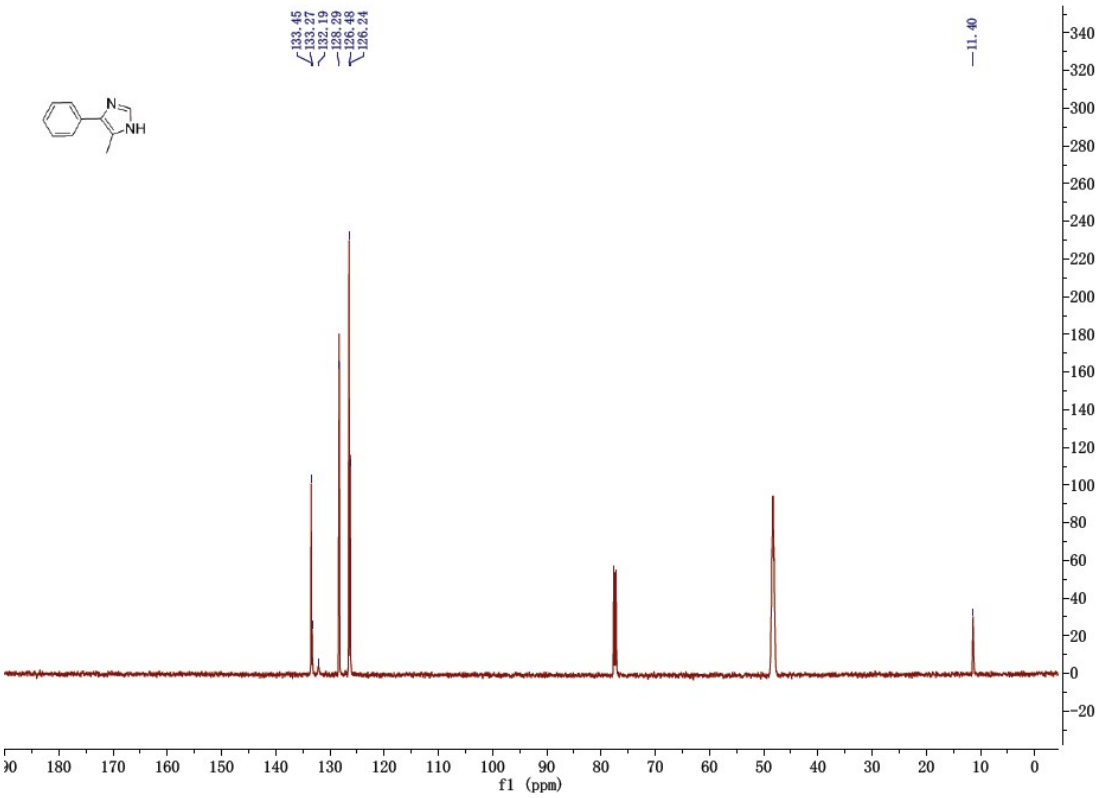
2.08
1.03
3.00
f1 (ppm)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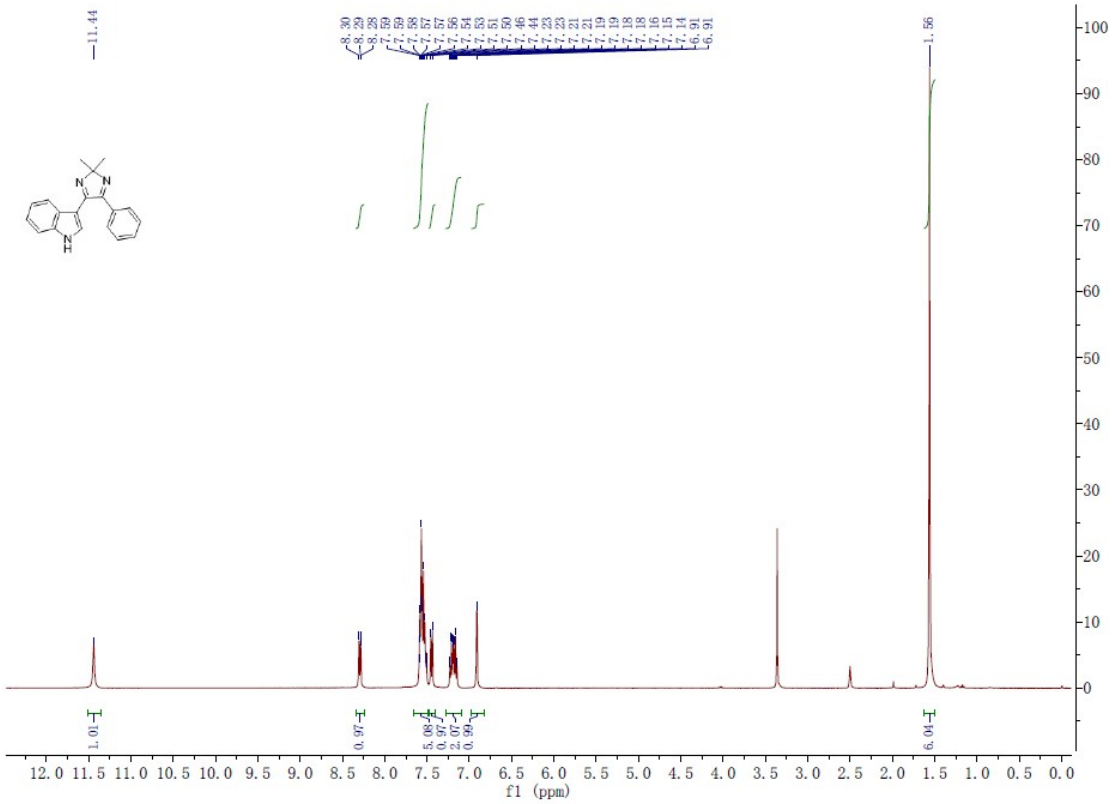
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7.51
7.50
7.46
7.44
7.23
7.22
7.21
7.21
7.19
7.19
7.18
7.18
7.16
7.15
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6.91
1.56
1.01
0.97
5.08
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2.07
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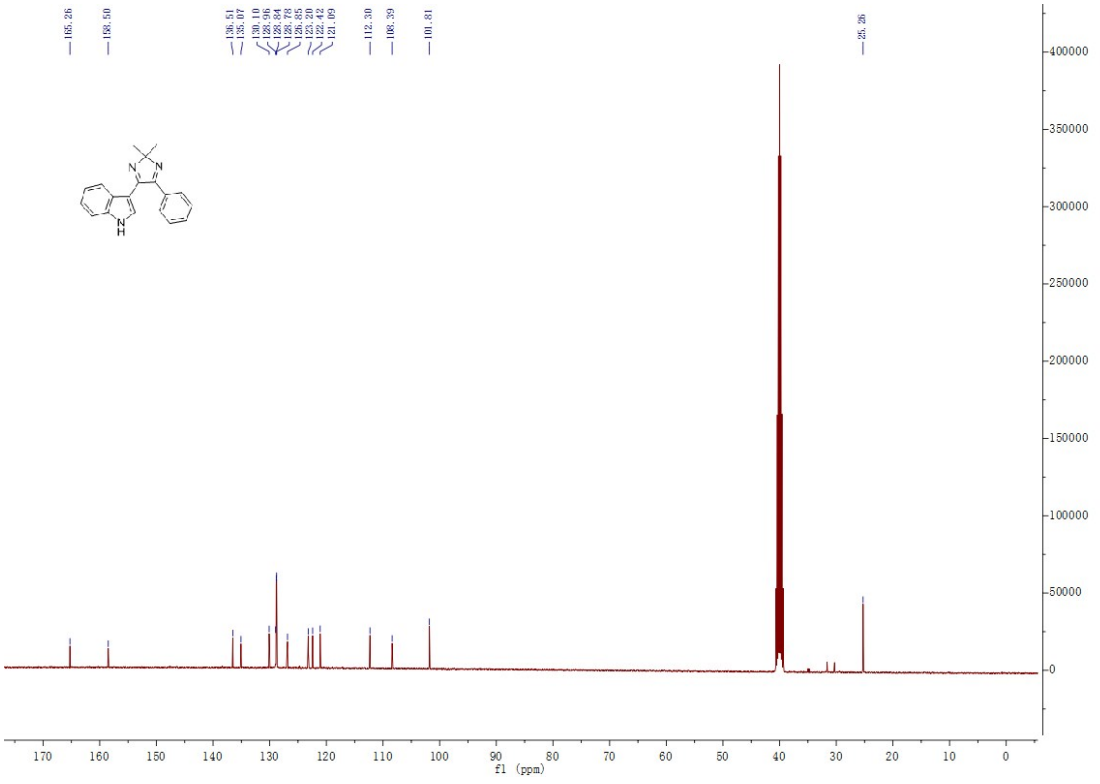
6.04
f1 (ppm)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121.09
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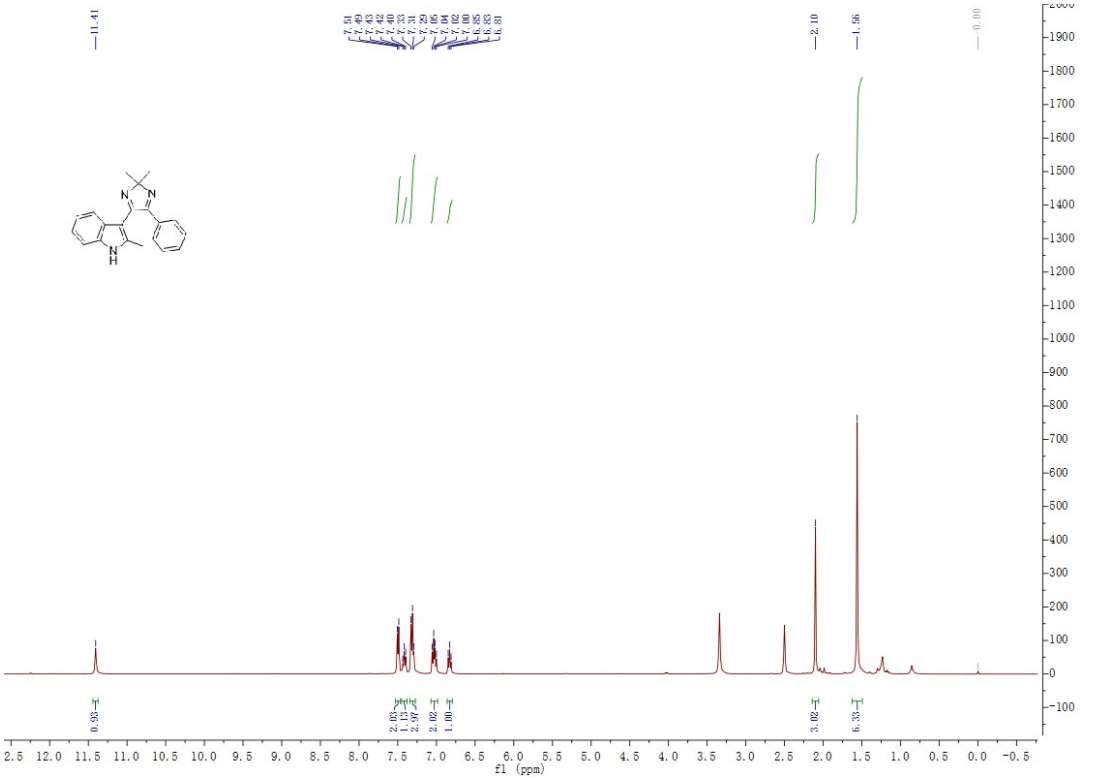
25.26
f1 (ppm)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7.00
6.85
6.83
6.81
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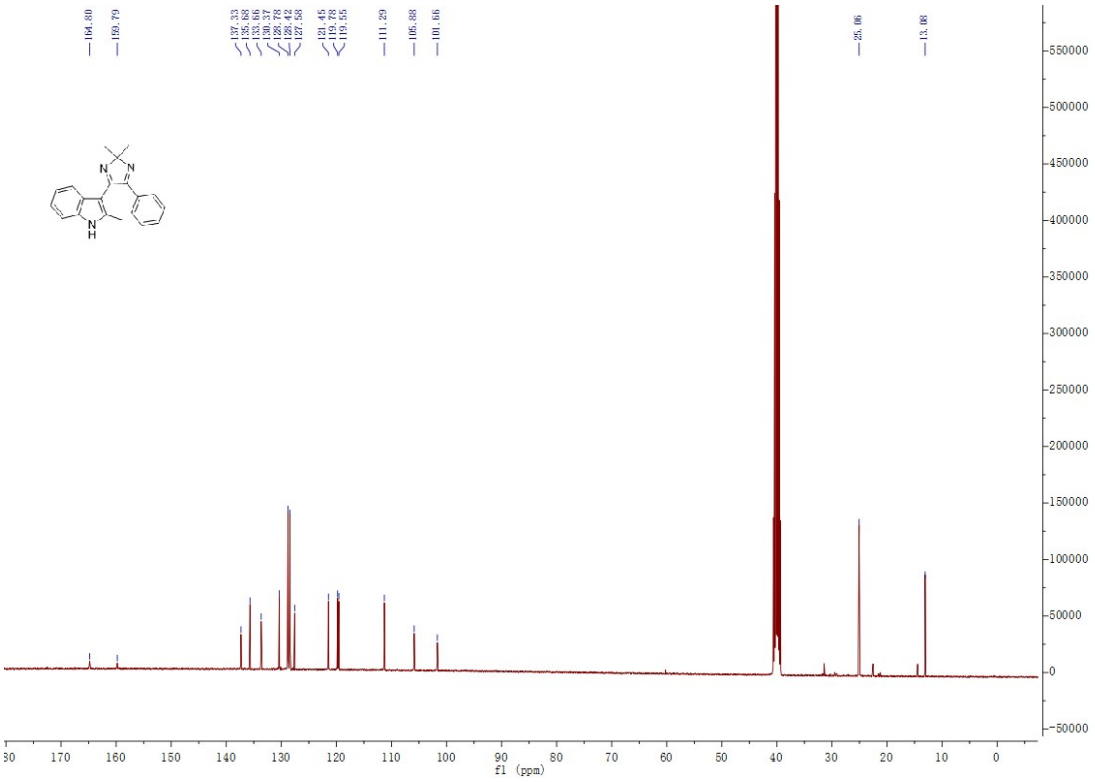
1.13
2.97
2.02
1.00
3.02
6.33
f1 (ppm)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111.29
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101.66
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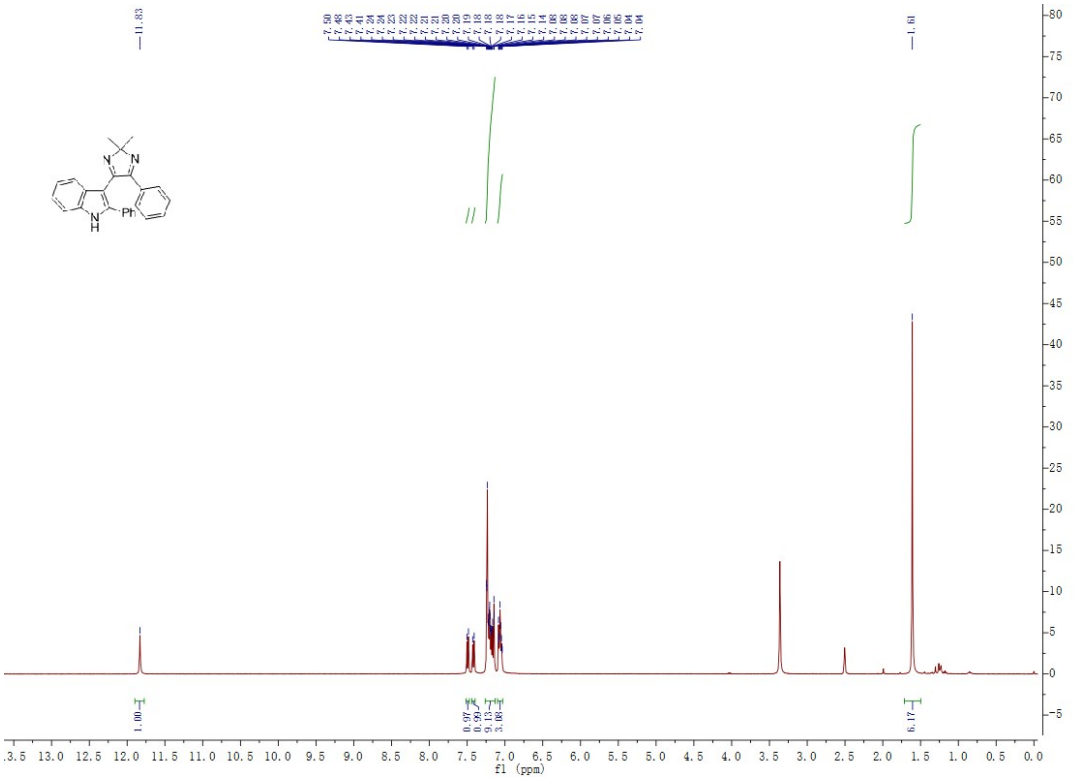
13.88
f1 (ppm)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7.18
7.17
7.16
7.15
7.14
7.08
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7.04
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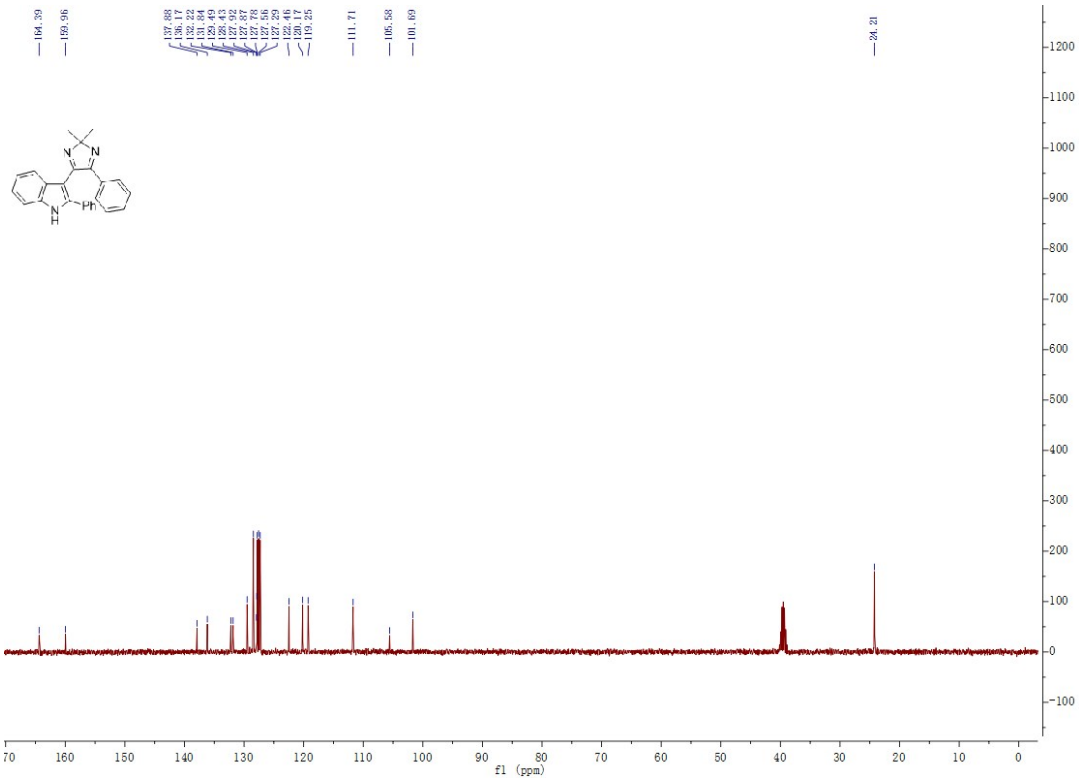
9.13
3.08
6.17
f1 (ppm)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120.17
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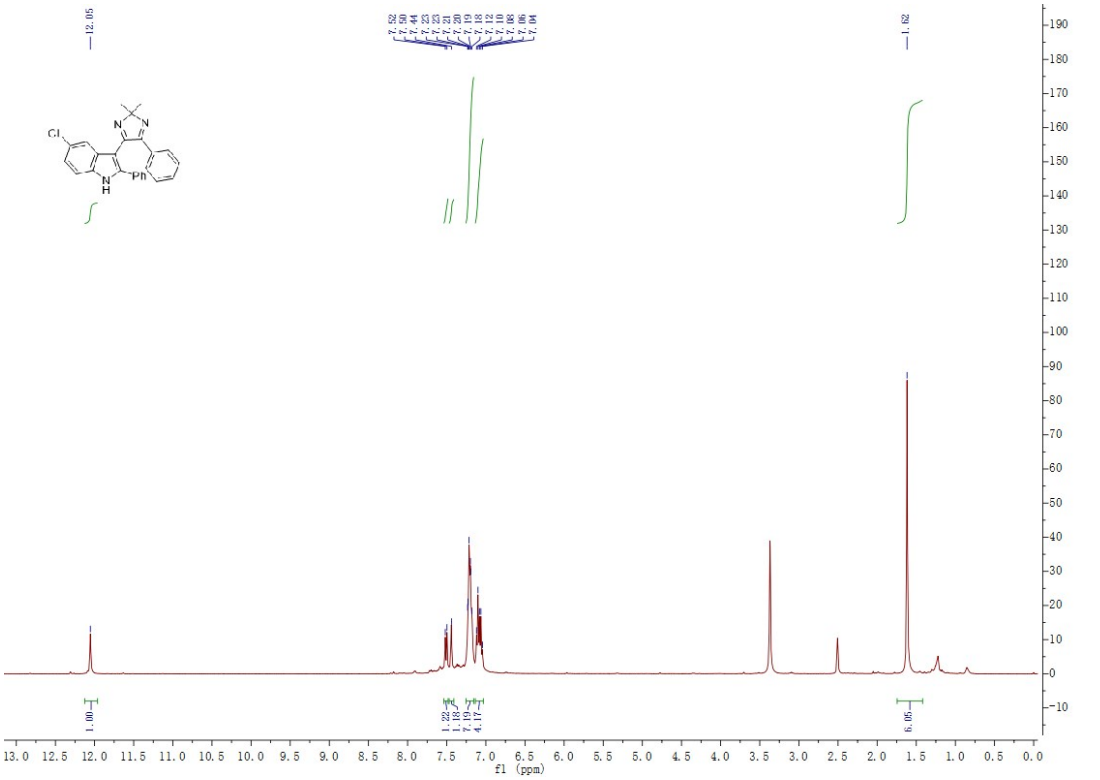
24.21
f1 (ppm)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7.10
7.08
7.06
7.04
1.62
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N
N
H
Ph
1.00
1.22
1.18
7.19
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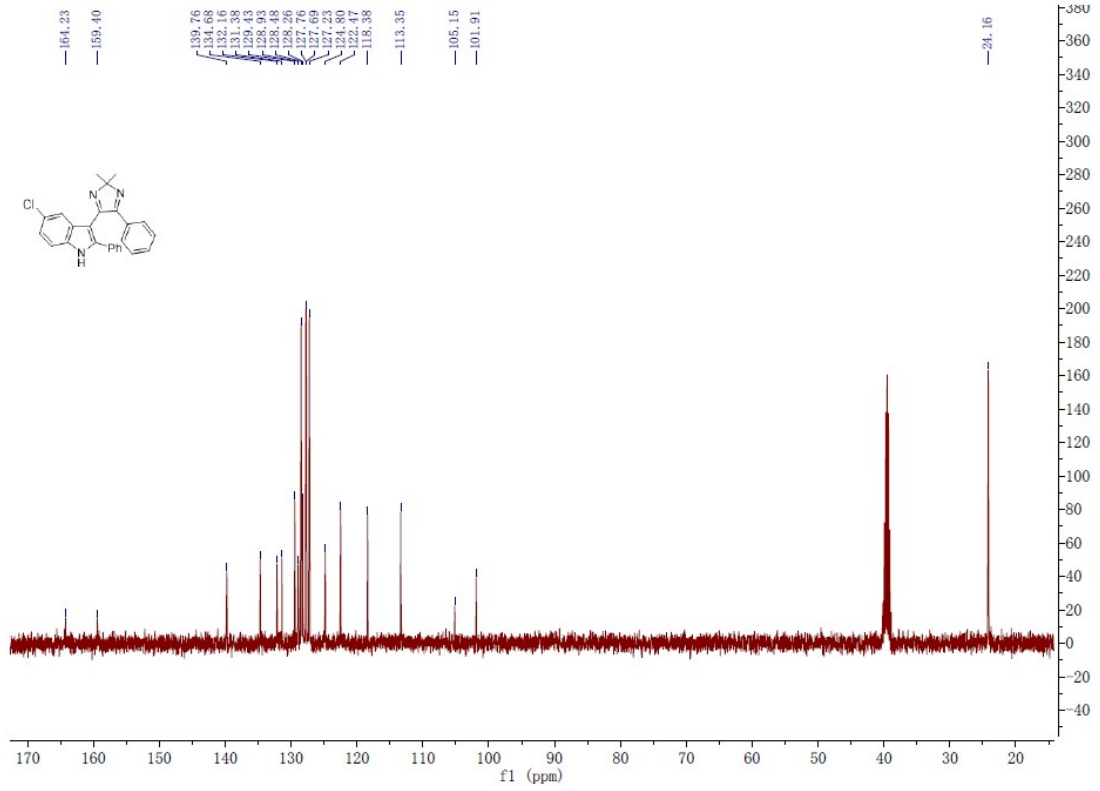
6.05
f1 (ppm)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127.23
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113.35
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101.91
24.16
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N
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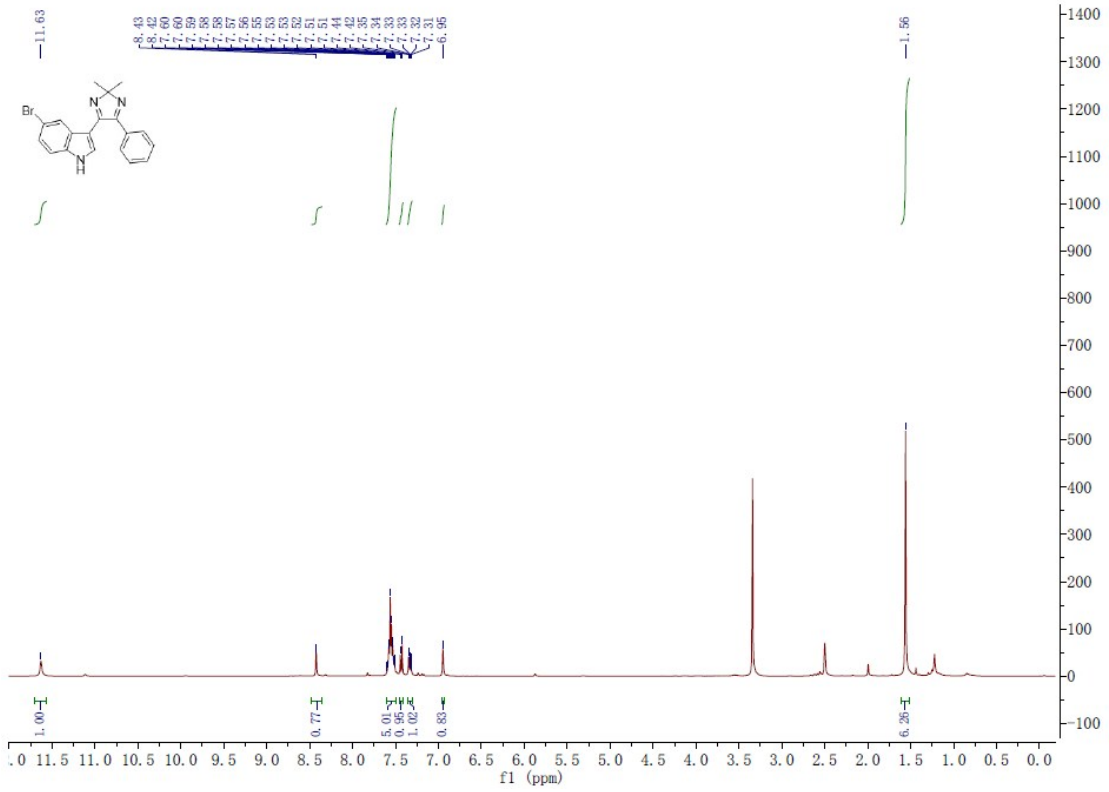
N
H
Ph
f1 (ppm)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7.34
7.33
7.33
7.32
7.31
6.95
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H
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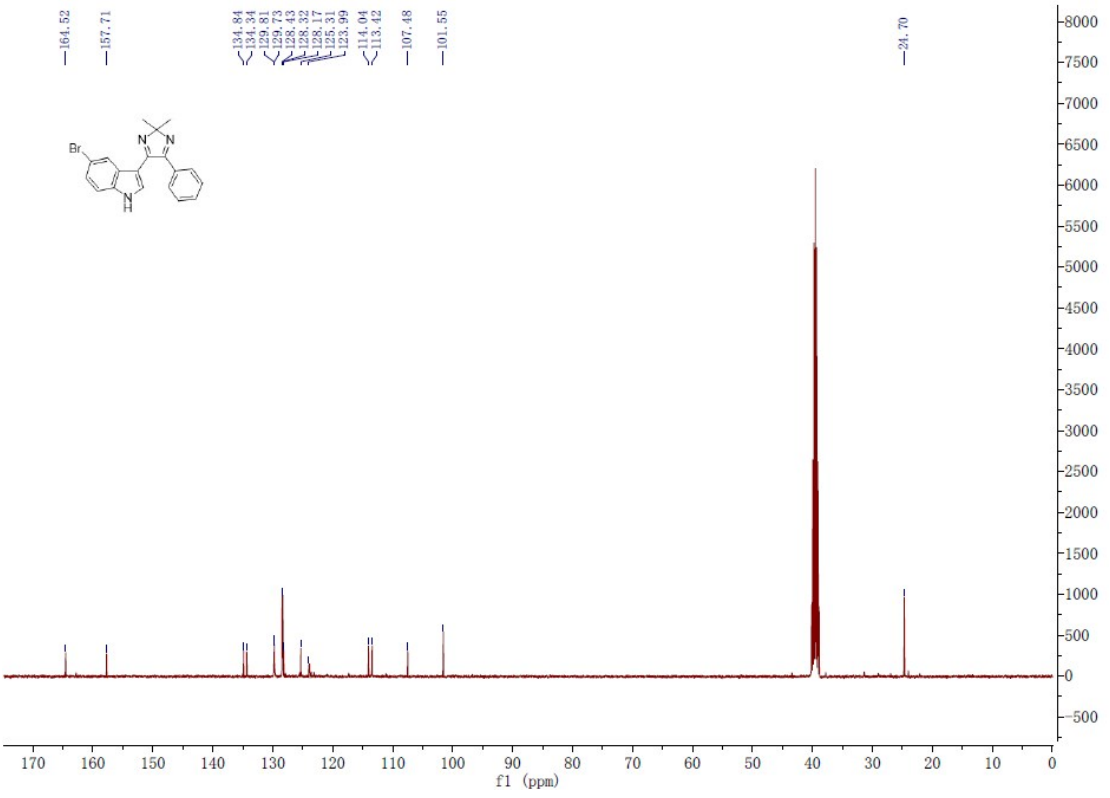
1.02
0.83
6.26
f1 (ppm)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107.48
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24.70
Br
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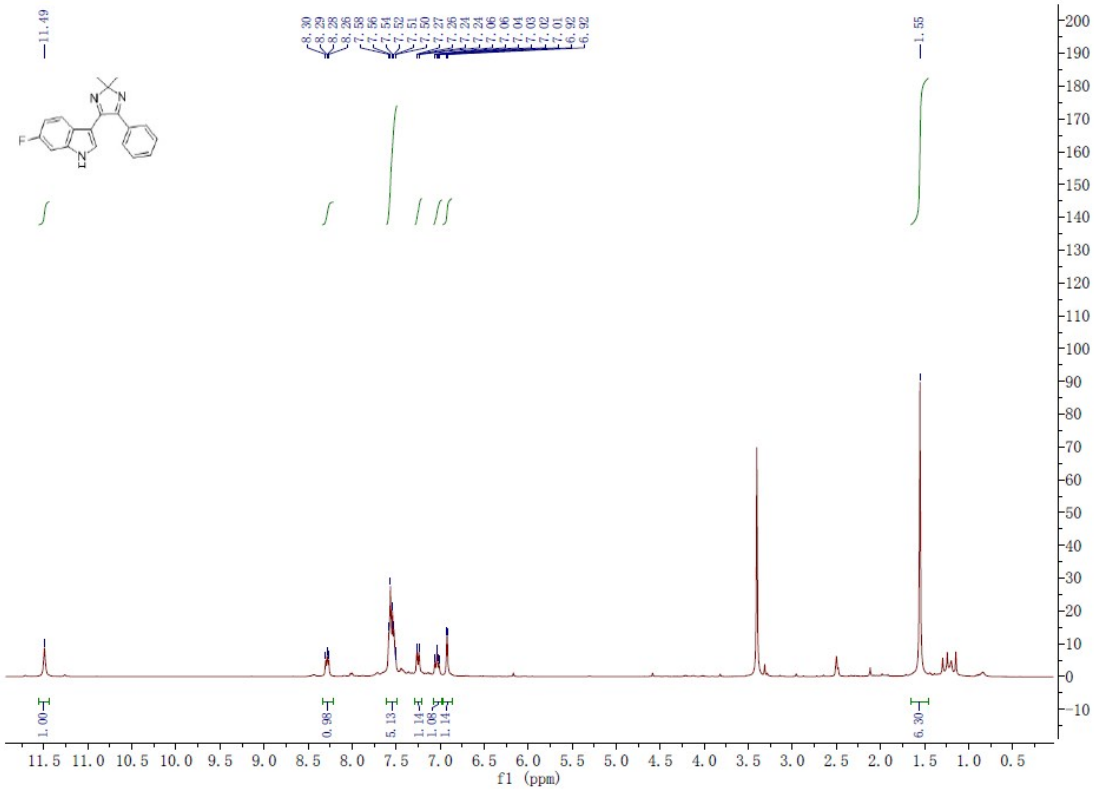
N
H
f1 (ppm)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7.24
7.24
7.06
7.06
7.04
7.03
7.02
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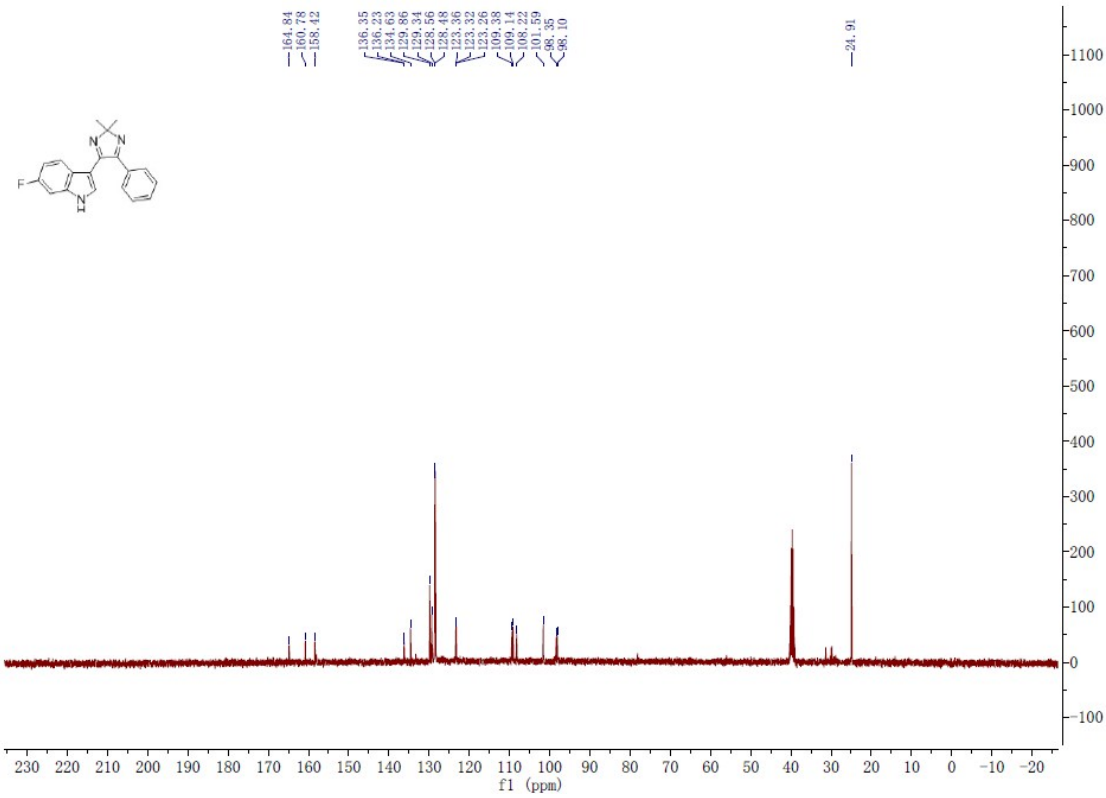
1.14
1.08
1.14
6.30
f1 (ppm)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108.22
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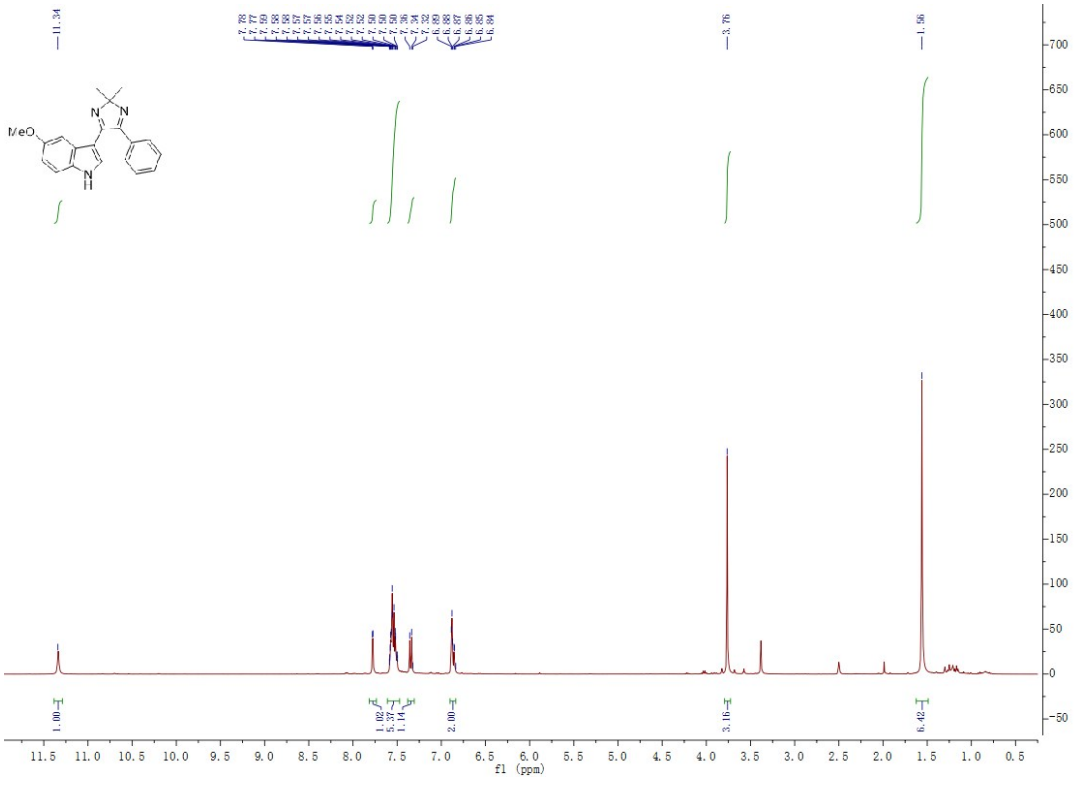
24.91
f1 (ppm)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7.34
7.32
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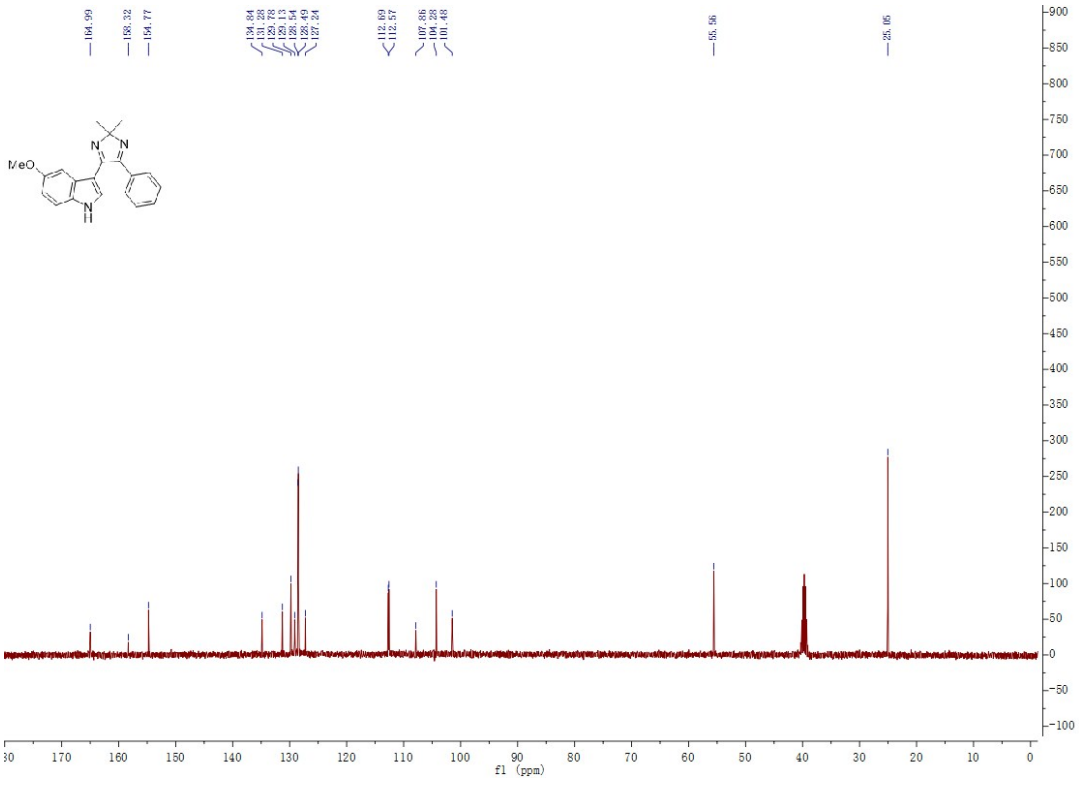
6.87
6.86
6.85
6.84
3.76
1.56
MeO
1.00
1.02
5.37
1.14
2.00
3.16
6.42
f1 (ppm)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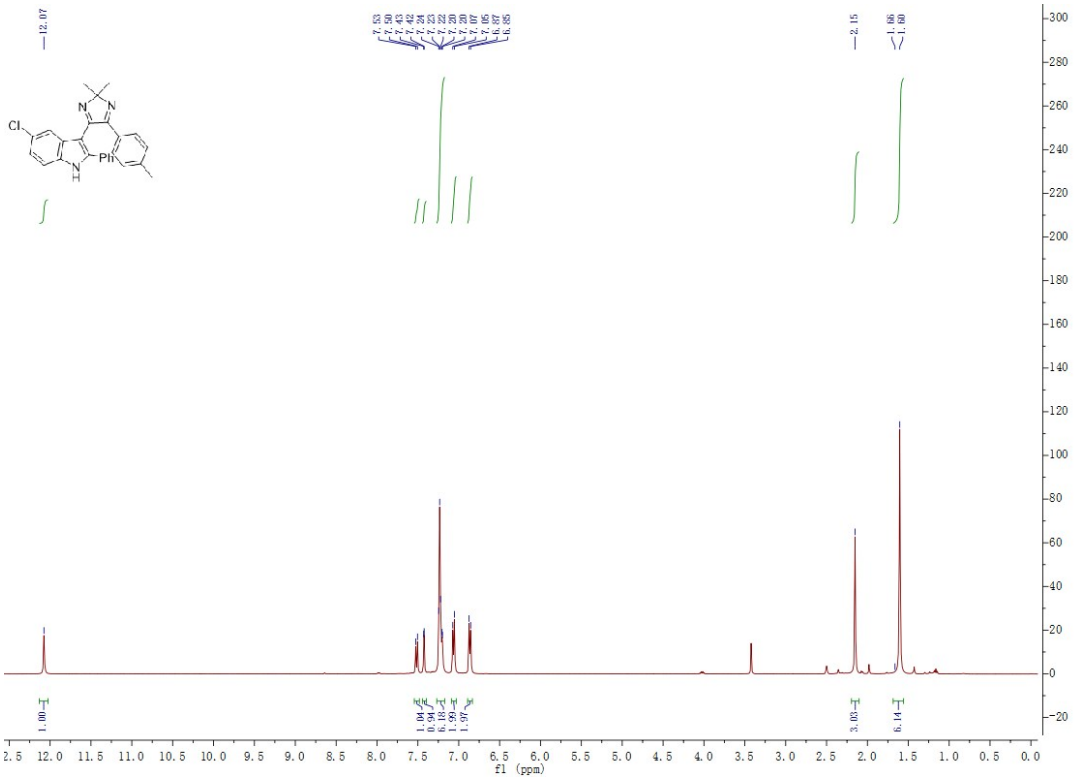
154.77
134.84
131.28
129.78
129.13
128.54
128.49
127.24
112.69
112.57
107.86
106.28
101.48
55.56
25.85
MeO
f1 (ppm)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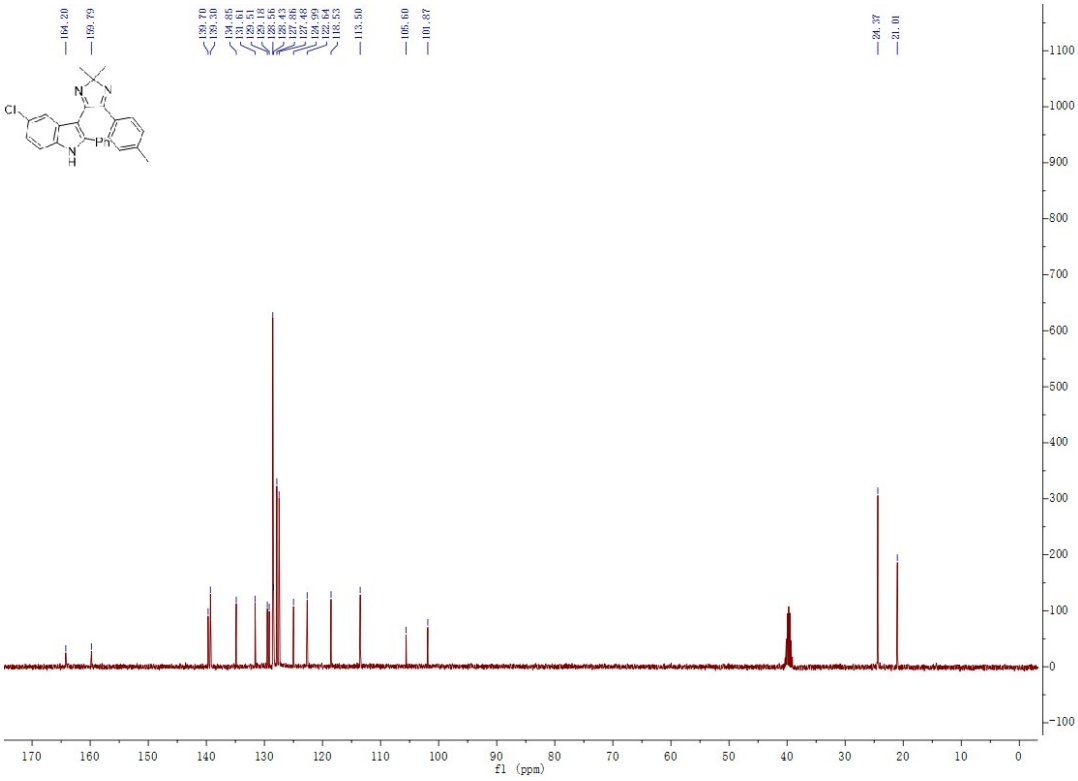
7.50
7.43
7.42
7.24
7.23
7.22
7.20
7.09
7.07
7.05
6.87
6.85
2.15
1.66
1.60
Cl
N
N
Ph
H
1.00
1.04
0.94
6.18
1.99
1.97
3.03
6.14
f1 (ppm)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129.51
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127.36
127.48
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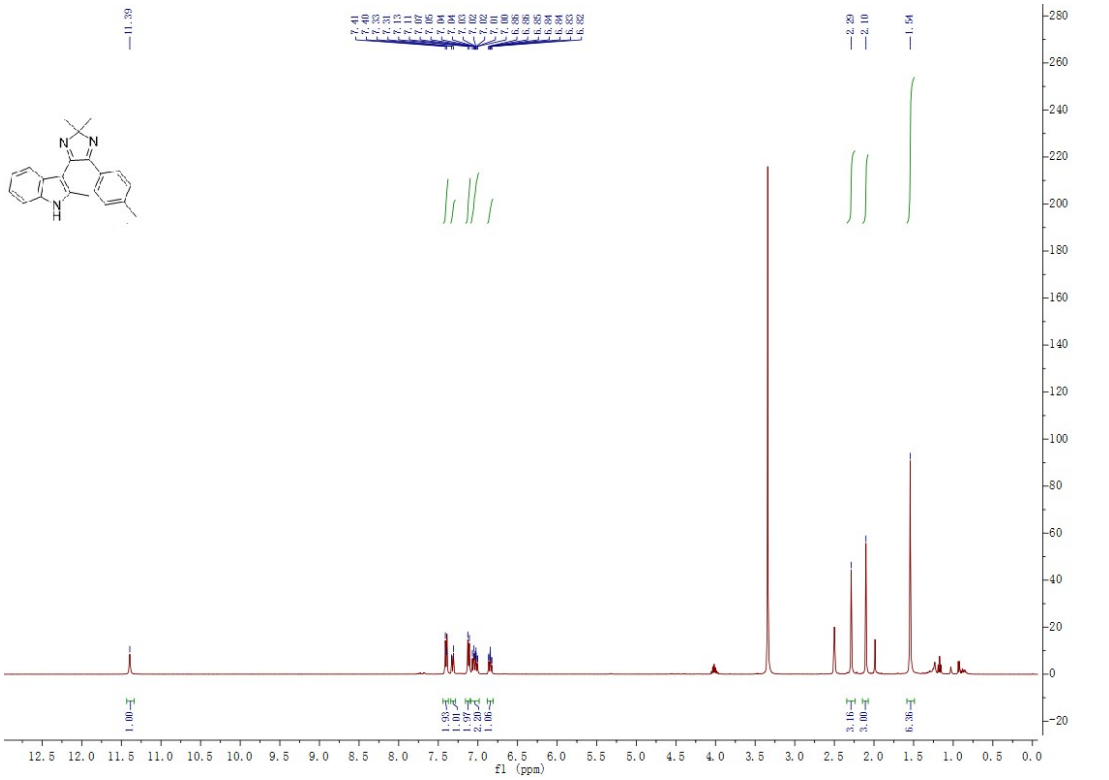
113.50
105.60
101.87
24.37
21.01
Cl
N
N
Ph
H
f1 (ppm)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7.40
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7.31
7.13
7.11
7.07
7.05
7.04
7.04
7.03
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7.01
7.00
6.86
6.85
6.84
6.84
6.83
6.82
2.29
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1.97
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2.06
3.16
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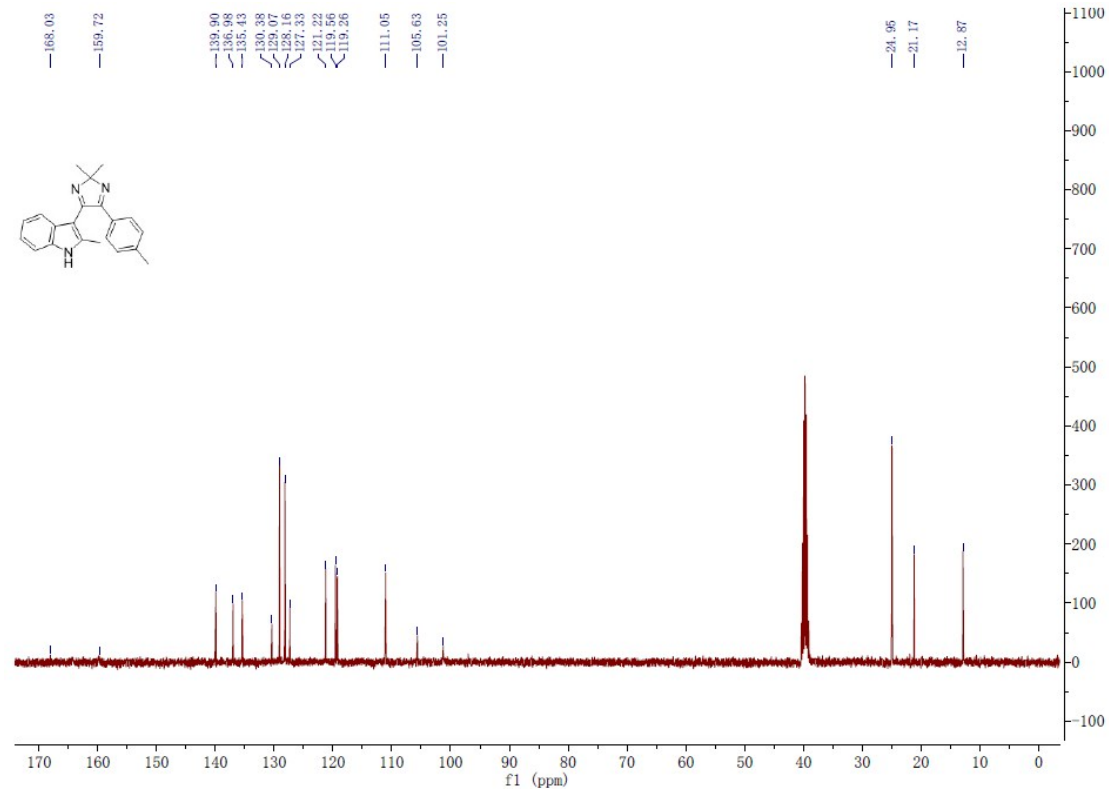
f1 (ppm)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159.72
139.90
136.98
135.43
130.38
129.07
128.16
127.33
121.22
119.56
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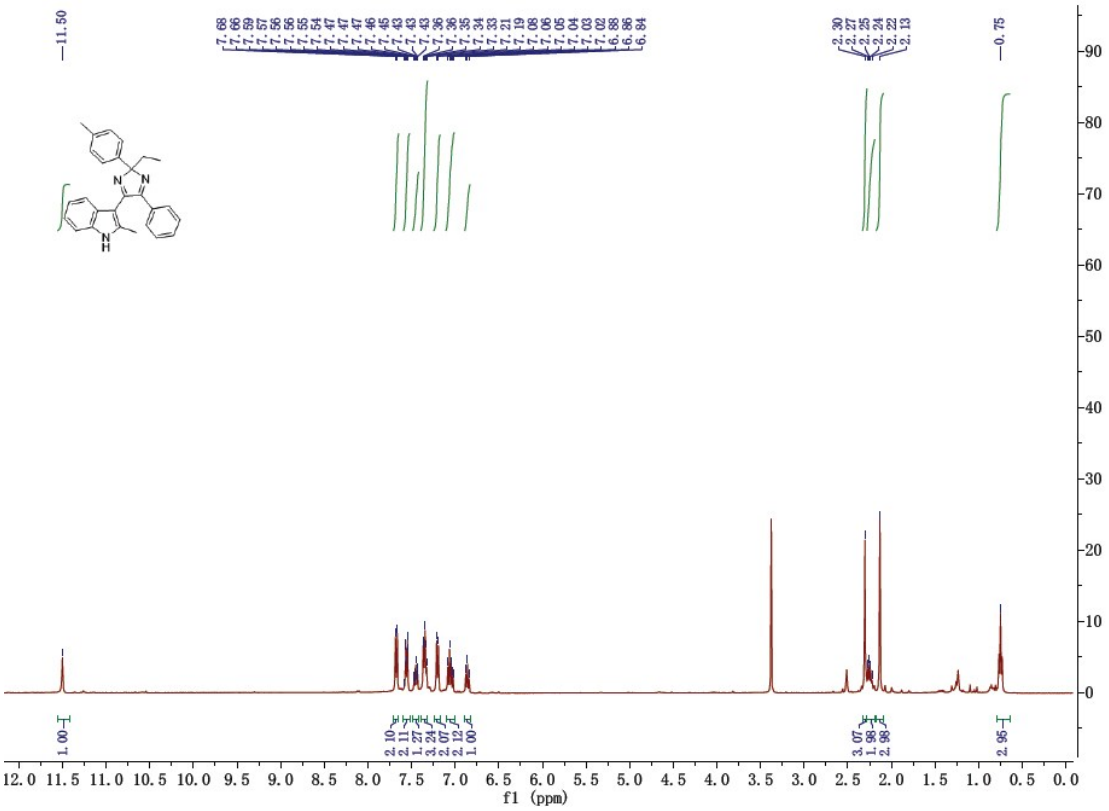
111.05
105.63
101.25
24.96
21.17
12.87
f1 (ppm)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7.56
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7.55
7.54
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7.47
7.47
7.46
7.45
7.43
7.43
7.43
7.36
7.36
7.35
7.34
7.33
7.21
7.19
7.08
7.06
7.05
7.04
7.03
7.02
6.88
6.86
6.84
2.30
2.27
2.25
2.24
2.22
2.13
0.75
1.00
2.10
2.11
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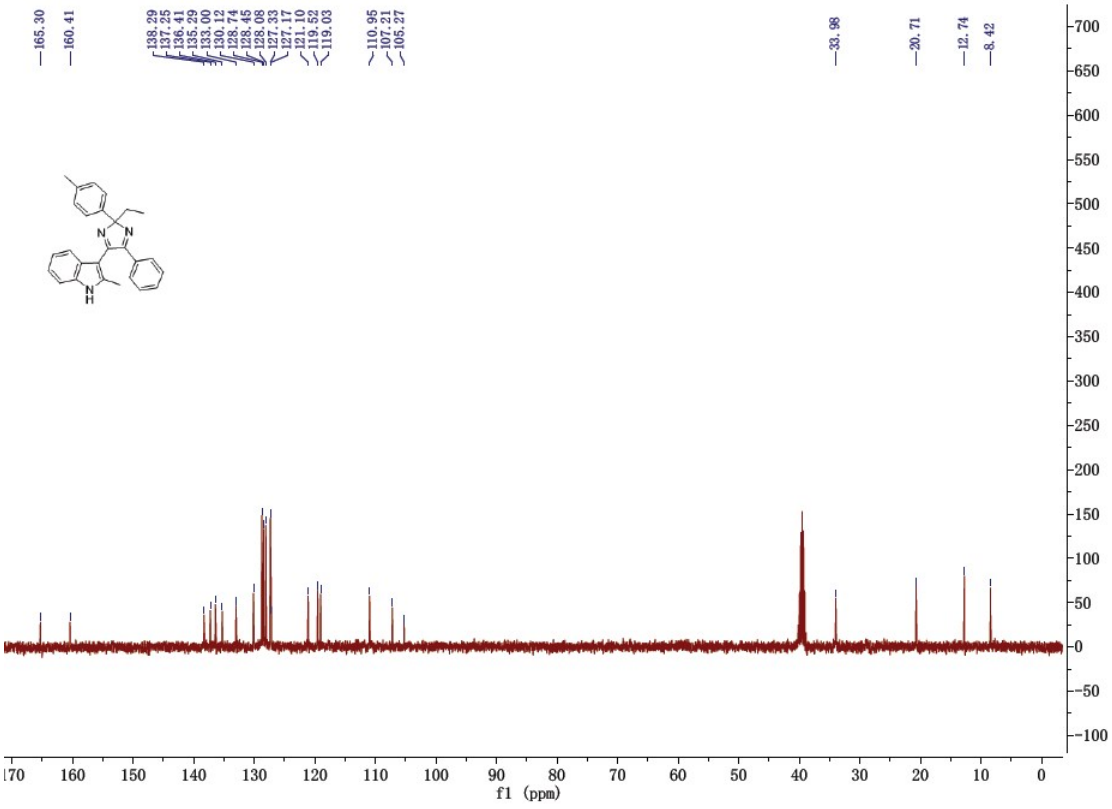
3.24
2.07
2.12
1.00
3.07
1.98
2.98
2.95
f1 (ppm)


165.30
160.41
138.29
137.25
136.41
135.29
133.00
130.12
128.74
128.45
128.08
127.33
127.17
121.10
119.52
119.03
110.95
107.21
105.27
33.98
20.71
12.74
8.42
f1 (ppm)